ANNE

3-F

(Murray)

RKP

E.C)

ELEMENTS

OF

CHEMISTRY.

BY

J. MURRAY,

LECTURER ON CHEMISTRY, AND ON MATERIA MEDICA
AND PHARMACY, EDINBURGH.

IN TWO VOLUMES.

VOLUME FIRST.

EDINBURGH:

PRINTED FOR WILLIAM CREECH, JOHN ANDERSON, AND
REID & BATHGATE, EDINBURGH; AND FOR
LONGMAN, HURST, REES, ORME & BROWN,
AND T. UNDERWOOD, LONDON.

1810.

TO THE BINDER.

The Plates to be put at the end of the First Volume.

NOTICE.

I have not announced this work as the second edition of the Elements of Chemistry, which I formerly published, as from the rapid progress of the Science, it has been necessary to write it nearly anew. Its object, however, is the same,—to give such a view of Chemistry as shall convey a just knowledge of its leading principles and more important facts, without including the discussion of controverted opinions, or the statement of those minute details which have with propriety a place in a Systematic Work.

Edinburgh, }
October 25. 1810. }

CONTENTS OF VOL. I.

INTRODUCTION.

GENERAL VIEW OF THE NATURE, OBJECTS, AND APPLICATIONS OF CHEMISTRY. HISTORICAL SKETCH OF ITS ORIGIN AND PROGRESS. PRINCIPLES OF CHEMICAL ARRANGEMENT.

THE different departments of Physical Science have relations more or less intimate, whence it becomes difficult to establish their respective limits with perfect precision. Still there are certain leading characters by which the classes of phenomena, which it is their object to investigate, may be discriminated, and the sciences themselves sufficiently defined.

One extensive class includes the phenomena which arise from actions exerted between masses of matter at sensible, and often at immense distances, accompanied in general with no other change than that of place, and, in particular, not connected with any alteration in the properties of the bodies between which they have been exerted.

Actions of this kind, under different modifications, constitute the various branches of MECHANICAL PHILOSOPHY. Astronomy has for the objects of its inquiries, the movements of the heavenly bodies. Optics studies the phenomena which arise from the motion of the rays of light. To Pneumatics belongs the consideration of the impulse, pressure, and resistance of elastic fluids: and under Mechanics, in the extensive sense of the term, is placed the determination of the effects of the same forces on non-elastic fluids and solids. In all of these, the changes which are the objects of investigation are the results of sensible motions arising from the operation of powers which act at perceptible distances; they are therefore capable of being determined with precision; and hence a leading character of these sciences, that their principles can be established on mathematical evidence.

Another class of actions of a very different nature, comprises those which are exerted between the minute particles of matter. We are liable, in regarding any solid body, to consider it as a continuous mass, all the parts of which are in perfect contact. A little inquiry, however, is sufficient to convince us of the error of this conclusion, and to prove to us that every mass of matter, even in its densest state, is composed of minute particles, which are not in contact, but are only retained within certain distances by a peculiar force. We soon discover, too, that this force is liable to be variously modified, and that in consequence of this, these particles are capable of acting on each other, of changing their relative positions, and of entering even into intimate combinations. Hence arises an exten-

sive class of actions, more obscure and complicated than those which belong to the Mechanical Sciences. The investigation of these actions constitutes the Science of CHEMISTRY.

Chemical action is thus distinguished by characters sufficiently marked. It is exerted between the minute particles of matter: it brings them into new arrangements or combinations, whence changes are produced in the properties of the bodies subject to it; and being exerted at no sensible distances, it admits of no precise determination, as to its direction or intensity, but is discovered only from changes of constitution or of form. And Chemistry, in conformity to these views, may be defined, the Science which investigates the combinations of matter, and the agencies of those general forces whence these combinations are established and subverted.

The principal power productive of chemical phenomena, is that species of ATTRACTION, exerted between the particles of bodies, which brings them into intimate and permanent union. From its exertion between particles of a similar nature, arise the forms under which bodies exist, and many of the physical qualities of which they are possessed. And from its exertion between particles of different kinds, are derived the greater number of substances which compose our globe,—these consisting of certain elements retained by this power in a state of combination.

This attractive force is always modified in its action by certain repulsive powers. Of these the most general is the power of Heat. Its immediate operation is to separate the particles of bodies, and place them at greater distan-

ces; it thus changes their forms and qualities, and, when in a certain degree of intensity, subverts the combinations which attraction has produced. Galvanism is perhaps to be regarded as a force of a similar kind, or rather it communicates to the particles of matter both attractive and repulsive powers, whence similar changes of combination arise.

From actions so extensive and important, arise changes in the structure and constitution of bodies, connected with many of the established operations of nature, or capable of being adapted to purposes of utility, constituting various arts. Of these applications of Chemistry, a full development, even under a general point of view, would be incompatible with the limits of this preliminary discourse; but a few examples are required to convey a just idea of the extent of the science, and of the interest which its study is calculated to excite.

No view of adjustment in the economy of nature is more admirable than that which Chemistry traces with regard to the temperature of the globe, the sources of its variations, and the limits within which these are restrained. That degree of heat which is necessary to sustain the greater number of natural operations, is derived from the action of the solar rays on the surface of the earth; but from the mode in which this is communicated, it is necessarily unequal, or prevails in different degrees of intensity at different seasons, and at different regions of the earth; and did not certain arrangements exist, this inequality would continue progressive. These arrangements Chemis-

try unfolds, and by discovering that absorption of heat which attends the rarefaction of the atmosphere, the evaporation of water, and the melting of ice, and that evolution of heat which accompanies the reverse changes, it enables us to trace the causes by which the extremes of climate and the transitions of seasons are moderated, and the temperature over the surface of the globe is preserved within comparatively a limited range.

Chemistry has still to investigate another adjustment in the economy of nature, the necessity for which the researches of this science have alone discovered. That air is indispensable to living beings, is sufficiently demonstrated by familiar facts; but that this air, in being breathed by animals, is rapidly deteriorated, and rendered at length unfit to sustain life, is established by the experiments of the Chemist; and it is only by these experiments that the change of composition from which this arises is made known. It is of course only from the successful prosecution of these researches that we can discover the natural operations by which it is counteracted, and the due purity of the atmosphere preserved.

The spontaneous evaporation of water, its elevation in clouds, and its deposition in the form of dew, rain and snow, are dependent on chemical action. From the principles of this science, the laws which regulate these processes, so far as they are known, have been illustrated, and it is only from the extension and more strict application of these principles that their theory can be fully developed.

We trace the chemical agency of water in many other natural operations, in its action, for example, on the surface

of the earth, the disintegration it occasions, and the ultimate formation of soil; and in the processes of animated existence, particularly in sustaining the growth of plants, and affording the principles whence their products are formed.

By discovering to us, that the substances which belong to the Mineral Kingdom are compounds of certain elements, Chemistry demonstrates that their formation must have been the result of chemical combinations; and the application of its principles must afford the explanation of those arrangements, which the observations of the Geologist, skilfully generalized, have demonstrated to prevail in the structure of the solid parts of the globe. And it will also ultimately give the only sure basis on which the *species* of minerals are established and arranged.

We can trace the predominance of chemical action, not less in the processes of animated nature, though these, from their obscurity and complication, are more difficult of elucidation. In vegetation we discover a series of operations, in which the principles conveyed to the growing plant are brought into new combinations, so as to form its diversified products: some of the chemical agencies connected with it have been already successfully investigated; and in the progress of the science we may, without any undue confidence, predict its full development, as a result of chemical affinities, modified by the circumstances under which they are exerted. The chemical processes of the Animal System are still more complicated and more dependent on, or at least more intimately connected with, the peculiar laws of vitality; yet even in these, Chemistry has discovered a number

of important truths: the most perfect theory which we yet have of any function of life, that of respiration, and the production by that process of animal heat, is strictly chemical, and affords a proof of what may be attained in a more advanced state of chemical physiology.

With the processes of Art, Chemistry is not less strictly connected than with the operations of Nature; nor would it be easy, in an Introductory Sketch, to do justice to its practical applications. The extraction of metals from their ores, the purifying, casting, and forging them, the production of metallic alloys, and of metallic pigments, the manufacture of glass, of pottery and porcelain, the processes of bleaching and of dyeing, of making starch, sugar, and vinegar, of fermenting and distilling, of tanning, of soap-making, and of preserving animal substances from putrefaction,—all of these, in their most minute details, are in the strictest sense of the term Chemical Operations. It is from the skilful application of the principles of this science, rather than from the uncertain suggestions of chance or of random experiment, that their improvement is to be derived. As Chemistry advances, its applications to purposes of utility will become more extensive, and more easily regulated; and as it is unbounded in the objects of its researches, we can assign no limits to the extent of these relations, nor foresee how far it may yet add to the power of man.

This important department of Physical Science is altogether of modern origin. It had no place in the system of Ancient Philosophy; and though arts were practised from the most remote antiquity, the processes of which are dependent on chemical actions, the relations of these were never discovered, and their principles remained unknown.

Its origin is to be traced to a singular pursuit which commenced towards the decline of literature, and which continued for many ages to be followed with unabated ardour,—that of the art of transmutation, or of converting the baser metals into silver or gold. In the prosecution of these delusive researches, observations were necessarily made on the changes produced by the mutual chemical actions of bodies, and these formed the base on which the science of Chemistry has been gradually reared.

The date of the rise of Alchemy, as this pretended art of transmutation was named, is not exactly known. It has been traced to the fifth, the fourth, or even to the third century; but there is every reason to doubt of the authenticity of the authorities on which it has been referred to these early periods. Towards the close of the fifth century, some progress appears, however, to have been made in chemical, or rather alchemical investigations. Among the Arabians, who had received the science and literatur of the Greek Empire, the study of alchemy was eagerl prosecuted; and transferred to Europe, it continued am the darkness of the middle ages, and even to a later riod, to delude and mislead those who endeavoured t netrate the mysteries of nature. The ultimate failu

these laborious researches led to the suspicion of the soundness of the views from which they originated; and the real, though slow progress of experimental inquiry, enlightened by the more philosophical spirit of investigation which marked the sixteenth century, banished at length the follies and deceptions of alchemy, and laid the foundation of chemical knowledge. At the conclusion of this period, a number of important facts had been established; some of the most powerful chemical agents had been discovered; the instruments of the principal operations of Chemistry were invented, and the methods of conducting its processes were improved.

It is not the object of this sketch to follow with any minuteness the progress of Chemistry through its successive stages. It is sufficient to give it a more rapid glance. Kunckel, Homberg, Lemery, and Geoffroy, were its first eminent cultivators free from alchemical bias. Van Helmont had called the attention of Chemists to the aërial fluids so frequently disengaged in their experiments, and had even pointed out some of their properties and distinctions,—a subject prosecuted by Boyle, especially in so far as related to the action of atmospheric air, and by Mayow, with still more extensive and accurate views. Bacon fixed the limits of Chemistry, and assigned it its due rank in the scale of natural knowledge; and Newton generalized its principal phenomena, by tracing more distinctly the combinations and decompositions, which are the chief objects of its investigations, to the operation of that species of attraction exerted at insensible distances between the particles of matter.

Beecher sought to anticipate what is the final object of chemical investigations, and what will only be attained when these have reached perfection,—the determination of the elements from the combination of which all the existing varieties of matter are formed: and Stahl, adopting in part his views, but limiting his speculations to the operation of one principle, that to which the property of communicating inflammability was ascribed, framed an hypothesis so extensive in its chemical relations, as to have been regarded at one time as a general system of the science, and so well constructed as to have commanded unlimited assent.

The process of Combustion is of primary importance in Chemistry, not only from the striking phenomena it displays, but from its affording in some measure a division of bodies founded on chemical relations, and from giving origin to some of the most important chemical agents. Changes analogous to those which occur in this process, are likewise produced by the operation of these agents; and thus, whatever theory is framed of combustion itself, is farther extended, and is indeed capable of being more or less remotely connected with nearly the greater number of chemical phenomena. Stahl supposed the existence of a common principle, Phlogiston, as he named it, in inflammable bodies: its disengagement, under the form of heat and light, constituted, he imagined, the process of burning: its escape gave rise to the change of properties, and particularly to the loss of inflammability, which the body suffering combustion always sustains: its communication again to the burnt body restores its original quali-

ties; and its transfer, in other cases of chemical action, gives rise to analogous effects.

This hypothesis connected a number of phenomena by a common principle, and apparently afforded a just explanation of them. Resting, however, on an imperfect knowledge of the facts which it generalized, the progress of the science discovered its imperfections, and established very different views.

Substances existing in the aërial form, are from their subtility apparently not easily subjected to the usual methods of chemical investigation; and hence, though some of the facts connected with their formation and disengagement had attracted the attention of Chemists, their chemical actions had never been clearly investigated, their distinctions established, nor the importance of their agency understood. Black, by his discovery of the properties and combinations of one of these aërial substances, Fixed Air, or Carbonic Acid Gas, demonstrated the importance of these researches, and the department of Pneumatic Chemistry was soon eagerly cultivated. By the discoveries of Cavendish, Priestley, and Scheele, the existence of other aërial fluids, their properties, and chemical relations, were established: and Lavoisier, entering the same path of experiment, and availing himself of these discoveries, advanced speculations distinguished by their novelty and ingenuity, and which soon assumed the place of the hypothesis of Stahl. The phenomena which had been ascribed to the evolution of phlogiston, Lavoisier proved to arise from the combination of the base of an aërial fluid, Oxygen, which forms the most active principle of atmospheric air.

He traced the chemical agencies of this principle, and framed a system seducing by its simplicity, resting apparently on a just induction, supported by experiments distinguished by precision, and which, after a short period of animated discussion, was universally received.

At the close of this period, Chemistry, it was imagined, had nearly attained perfection, or at least it was supposed that little more than insulated facts remained to be made known. A short time has been sufficient to demonstrate the narrowness of these views. The laws of chemical affinity, which had been regarded as established by Bergman, have been materially modified by the researches of Berthollet; views altogether novel have been presented, and the theory of chemical action rendered more precise in its minute details. And the acquisition of a new instrument of chemical analysis, in the power of Galvanism, has already, in the discoveries of Davy, subverted or rendered doubtful much of the established system, and opens a career of investigation, the limits of which no imagination can define. The science is probably only in its infancy: it is at least far distant from that maturity, if this shall ever be reached, when its ultimate object shall be attained, when the real elements of bodies shall have been detected, and all their modifications traced: we know nothing of its real extent; nor can we, from our present knowledge, form any just conception of the stages of discovery through which it has to pass.

The last object in this introductory sketch is to state the principles on which the arrangements of Chemistry are formed.

The investigations of this science being directed to the actions which are exerted among the particles of matter, in consequence of which they pass into new arrangements and new states of combination, and these actions arising from the operation of certain general forces, it obviously divides itself into two great departments,—the first comprising the investigation of the general effects and laws of these forces; and the second considering their operation on individual substances. Under the former are placed the doctrines of Attraction, and of its antagonist force Repulsion, as produced by the operation of heat, light, and electricity; to the latter belongs the history of the chemical properties, and combinations of all known bodies.

The first of these divisions admits of little diversity of arrangement, nor is it of much importance in what order the subordinate parts belonging to it are placed. The second presents much greater difficulties, and hence the numerous systems of chemical classification that have been proposed.

Two general methods are suggested by the nature of the science itself. Its object is to discover the composition of bodies, or, by analytic operations, to resolve them into the principles of which they are composed. The necessary result of such investigations, is, that substances are arrived at beyond which the analysis cannot be carried. In the theory of Modern Chemistry these are regarded as

simple; they are characterized by their most striking properties, and their combinations are investigated.

Now it is obvious, that in forming a system of chemical classification, we may, following the synthetic mode, assume these simple substances as the basis of the arrangement, and place their compounds in a determinate order, according to their composition. Or we may follow the reverse method: we may arrange the substances, which are presented to us by nature, into orders founded on analogies in chemical properties; and from the history of such of them as are compounds, we may follow the results of analysis, and proceed to the history of their more simple principles.

Since the establishment of the system of Modern Chemistry, Chemists have in general given the preference to the first of these, the synthetic mode of classification. There is undoubtedly some advantage in placing the simple substances before the compounds which they form, and classifications on this principle have a more scientific form.

Had Chemistry attained maturity, a perfect synthetic arrangement might be constructed, which might also perhaps be best adapted to display the relations of the science. But while it continues progressive, this must be attended with such difficulties as to justify the adoption of the opposite method.

The radical imperfection of any arrangement in which certain substances assumed as simple form the basis of the system is, that the simplicity of these substances can never be demonstrated, and that the progress of the science ge-

nerally leads to the discovery that they are compounds. They are regarded as simple, only because we are unable to decompose them; but this may arise, not from their real simplicity, but from the imperfection of our knowledge, and of our instruments of analysis. Their composition is accordingly in general at length discovered, and whenever this happens, the basis of the classification is of course subverted, and a new class of substances, supposed to be simple, is again to be formed. But of the real simplicity of these, we have no better proof than of the former: the progress of discovery may, and probably will prove them to be compounds, and the whole system must be again changed. This fluctuation must continue until the ultimate principles of bodies are discovered,—a period from which Chemistry is at present far distant, and until then, no arrangement, founded on these principles, can be stable, but must perpetually fluctuate with the progress of discovery.

Another imperfection which attends synthetic chemical arrangements is, that the student, in entering on the study of the science, has presented to his attention substances with which he is not familiar, or rather which, generally speaking, are unknown to him. It is seldom that bodies occur in nature in their state of simplicity; natural substances are almost uniformly compounds; their elements, therefore, cannot be generally known, and the knowledge of them can only be arrived at by a long, and often a complicated train of investigation. This difficulty, too, must become greater as the science advances; for in proportion to the extent to which analysis

is carried, the ultimate principles which are discovered are more remote from the natural bodies at which the analysis has commenced. The present state of Chemistry, were it necessary to enlarge on this subject, affords ample proof of the justness of these observations; the composition of a number of substances, regarded as simple, having been very recently established, and their principles being substances before unknown, and which are capable of being discovered only by difficult and refined modes of investigation.

For the reasons now stated, it has appeared to me preferable to relinquish the strictly synthetic mode of arrangement, and to adopt one the reverse; to take substances as they are presented to us by nature, class them from analogies in their chemical properties, and thus form natural orders, the distinctions of which the progress of the science will not subvert. From these we may proceed, under each of them, to the history of their elements, so far as the analysis has been carried, and thus the beginner of the study is led, by the most natural method, from what is known to what is unknown, and can follow more distinctly all the steps of the investigation. In conformity to these views, the arrangement presented in the following table is formed.

TABLE OF CLASSIFICATION.

PART I.

OF THE GENERAL FORCES PRODUCTIVE OF CHEMICAL PHENOMENA.

OF ATTRACTION.

OF THE ATTRACTION OF AGGREGATION.

— CHEMICAL ATTRACTION OR AFFINITY.

OF REPULSION, AND THE POWERS BY WHICH IT IS PRODUCED.

OF CALORIC.

— LIGHT.

— ELECTRICITY AND GALVANISM.

PART II.

OF THE CHEMICAL PROPERTIES AND RELATIONS OF INDIVIDUAL SUBSTANCES.

OF ATMOSPHERIC AIR AND ITS PRINCIPLES.

OF THE CONSTITUTION OF THE ATMOSPHERE.

— OXYGEN.

— NITROGEN.

— ATMOSPHERIC AIR.

— THE CHEMICAL AGENCY OF OXYGEN IN ITS PURE FORM, AND AS IT EXISTS IN ATMOSPHERIC AIR.

OF WATER AND ITS BASE.

OF HYDROGEN.

— WATER.

OF ALKALIS AND THEIR BASES.

OF AMMONIA AND ITS BASE.

— POTASSA AND ITS BASE.

— SODA AND ITS BASE.

OF EARTHS AND THEIR BASES.

OF BARYTES AND ITS BASE.

— STRONTITES AND ITS BASE.

— LIME AND ITS BASE.

— ARGIL AND ITS BASE.

— MAGNESIA AND ITS BASE.

— SILEX AND ITS BASE.

— ZIRCON AND ITS BASE.

— GLUCINE AND ITS BASE.

— ITTRIA AND ITS BASE.

OF ACIDS AND THEIR BASES.

OF NITRIC ACID AND ITS BASE.

OF NITRIC ACID.

— NITROUS ACID.

— NITRIC OXIDE.

— NITROUS OXIDE.

OF SULPHURIC ACID AND ITS BASE.

OF SULPHUR.

— SULPHURIC ACID.

— SULPHUROUS ACID.

— SULPHURETTED HYDROGEN.

— SULPHURETTED AND HYDRO-SULPHURETTED ALKALIS AND EARTHS.

OF CARBONIC ACID AND ITS BASE.

OF CARBON.

— CARBONIC ACID.

— CARBONIC OXIDE.

— CARBURETTED, AND OXY-CARBURETTED HYDROGEN GASES.

— CARBURETTED SULPHUR.

OF PHOSPHORIC ACID AND ITS BASE.

OF PHOSPHORUS.

— PHOSPHORIC ACID.

— PHOSPHOROUS ACID.

— PHOSPHURETTED HYDROGEN.

— PHOSPHURETTED SULPHUR.

OF MURIATIC ACID AND ITS BASE.

OF MURIATIC ACID.

— OXYMURIATIC ACID.

— HYPER-OXYMURIATIC ACID.

OF FLUORIC ACID AND ITS BASE.

OF BORACIC ACID AND ITS BASE.

OF METALS.

OF GOLD.
— SILVER.
— PLATINA.
— IRIDIUM.
— OSMIUM.
— RHODIUM.
— PALLADIUM.
— QUICKSILVER.
— COPPER.
— IRON.
— LEAD,
— TIN.
— ZINC.
— NICKEL.

OF COBALT.
— MANGANESE.
— ARSENIC.
— BISMUTH.
— ANTIMONY.
— TELLURIUM.
— CHROME.
— MOLYBDENA.
— TUNGSTEN.
— TITANIUM,
— URANIUM.
— COLUMBIUM.
— TANTALIUM.
— CERIUM.

OF THE NATIVE COMBINATIONS OF ACIDS, EARTHS, METALS AND INFLAMMABLES. MINERAL COMPOUNDS.

OF SALINE MINERALS.
— EARTHY MINERALS.
— METALLIC MINERALS.
— INFLAMMABLE MINERALS.
— THE NATURAL POSITIONS AND RELATIONS OF MINERALS, AND OF THEIR FORMATION.
— MINERAL WATERS.

OF VEGETABLE COMPOUNDS.

OF THE FORMATION OF VEGETABLE COMPOUNDS.
— THE CHEMICAL PROPERTIES AND RELATIONS OF VEGETABLE COMPOUNDS.
— THE SPONTANEOUS CHEMICAL CHANGES AND DECOMPOSITIONS OF VEGETABLE COMPOUNDS.

OF ANIMAL COMPOUNDS.

OF THE FORMATION OF ANIMAL COMPOUNDS.
— THE CHEMICAL PROPERTIES AND RELATIONS OF ANIMAL COMPOUNDS.
— THE SPONTANEOUS CHEMICAL CHANGES AND DECOMPOSITIONS OF ANIMAL COMPOUNDS.

PART I.

OF THE GENERAL FORCES PRODUCTIVE OF CHEMICAL PHENOMENA.

THE powers which operate in producing chemical action, are that species of attraction which is exerted at insensible distances between the particles of matter, causing them to pass into new arrangements and new combinations, and certain forces of repulsion, by which this attraction is counteracted, and these arrangements and combinations are modified or subverted. In proceeding to the consideration of these general forces, the most natural method appears to be to place first the doctrines of attraction, and after these to consider the operation of its antagonist powers.

There is some difficulty, it must be admitted, in considering the general doctrines of Chemistry before its particular details; for as these doctrines are inferred by generalization from individual facts, the former cannot be thoroughly understood, or their evidence clearly perceived, while the latter are unknown. Hence some Chemists have proposed to reverse this method. But the dif-

ficulty is in reality one unavoidable in either mode of arrangement; for it is equally impossible to give the chemical history of a single substance, without supposing a previous knowledge of the general phenomena and laws of chemical combination. In balancing the advantages of these methods, the first, it appears to me, will still claim the preference. It is possible to illustrate the general laws of chemical action by examples from substances familiarly known, or which, though unknown, are equally adapted to convey illustrations of abstract truths; and these laws being established, they may be developed and explained more minutely from the mutual actions of individual substances, while the history of these substances is given with more advantage, and can be rendered more complete, when the general doctrines have been previously delivered. There can scarcely be a heavier task, or one more calculated to damp the ardour of study, than to have to acquire the insulated facts of a science, unenlightened by any knowledge of the principles which unfold their relations.

BOOK I.

OF ATTRACTION.

Attraction is a term employed in philosophical language to denote that power or force by which the masses or particles of matter have a tendency to approach to each other, and to enter into more or less intimate contact or union. Different species of attraction have been observed, which give rise to different phenomena, and operate, so far as can be traced, according to different laws.

The attraction of gravitation is exerted at sensible, and often at immense distances, and between masses of the greatest size: its force, according to the law demonstrated by Newton, being directly as the mass or quantity of matter, and inversely as the square of the distance. The magnetic and electric attractions, though they give rise to peculiar classes of phenomena, so far coincide with the attraction of gravity, as to operate at sensible distances, and on masses of matter, and even, as has been attempted to be demonstrated, according to the same law.

Besides these, a species of attraction is exerted between the particles of matter, and at distances generally insensible. This force, when exerted between particles of the same kind, is named the Attraction of Aggregation or Cohesion: when exerted between particles of different

kinds, it is denominated Chemical Attraction, or Chemical Affinity. Both are concerned in the production of chemical phenomena, and the latter is the force on which all the combinations of matter depend.

Both have been supposed to be ultimately the same power; the differences in the results of their operation being referred with much probability to the difference of the particles on which they operate; aggregation uniting particles of a similar kind, and therefore producing, in each case, an aggregate possessed of similar properties; while chemical attraction, combining particles of different kinds, must give rise to products in which some modifications of properties must be the result. It has even been contended, that both of these are only modifications of that more general force which is exerted at sensible distances between the masses of matter; and the apparent differences in the laws which regulate their action from those which gravitation observes, have been ascribed to circumstances, which, in the one case, operate powerfully, while in the other they can have little effect. In the operation of contiguous attractions, the figures of the particles of bodies must, it has been conceived, have an important influence; while the figures of masses of matter, operated on at great distances, can give rise to no appreciable result. "Considering the vast distance," says Bergman, "we may neglect the diameters, and look upon the heavenly bodies, in most cases, as gravitating points. But contiguous bodies are to be regarded in a very different light; for the figure and situation, not of the whole only, but of the parts, produce a great variation in the effects of attraction. Hence

quantities, which in distant attractions might be neglected, modify the laws of contiguous attraction in a considerable degree."

This question is one which we scarcely can determine, since we are unable to estimate the force of those modifying circumstances which may exist; and the laws by which these attractions act, instead of being deduced from any assumption of the law of gravitation, must in the present state of the science be inferred from observation and experiment.

CHAP. I.

OF THE ATTRACTION OF AGGREGATION OR COHESION.

Aggregation has been defined, that power which unites particles of a similar kind. We perceive its action exemplified in a solid mass of matter, the parts of which cohere with a certain force, which resists any mechanical action that would produce their separation, and which, in different bodies, is exerted with very different degrees of strength. In liquids it appears to be weaker, or the parts are disjoined with much more facility: and in substances existing in the aërial form it is entirely overcome, the particles, instead of attracting, repelling each other. Bodies exist therefore in the solid, the liquid, and the aëriform

state, according to the force with which the attraction of aggregation is exerted between their particles, and it is this attraction which unites these particles together.

Aggregation in bodies is weakened or overcome by two causes; by the repulsion communicated by heat, or by the attraction which may be exerted by the particles of one body to those of another.

Heat communicated to a solid body separates its particles to greater distances, as is evident from the enlargement of volume which it produces. By thus increasing the distances, the force with which the attraction of aggregation is exerted, is weakened: if the application of heat be carried to a sufficient extent, it is so far weakened that the body passes into the liquid form; and if carried still farther, the attractive force is entirely overcome, repulsion is established between the particles, and the body passes into the aëriform state.

The same effects are produced by the exertion of that attraction which unites the particles of one body with those of another. If a liquid, for example, is poured on a solid substance, it often happens that the attraction exerted by the liquid to the solid is sufficiently powerful to subvert the cohesion of the solid; its particles are disunited to combine with those of the liquid, the solid diminishes in size, and at length entirely disappears. This forms the chemical process of Solution. A similar effect is sometimes produced by the chemical action of an aëriform fluid; and in some cases the mutual attraction, even of two solids, is such as to diminish the power of cohesion so far as to admit of their union, and their transition to a liquid state.

When these powers, whether of heat or of chemical attraction, are withdrawn, cohesion resumes its force; but with results which are different, according to the circumstances under which this happens.

When the attraction of aggregation is suddenly exerted, and with considerable force, the particles are united in general indiscriminately, and according to no regular law. If a body which has been melted is suddenly cooled to a sufficient extent, it becomes solid, without its particles being united in such a manner as to produce any regular structure or form. Or if its cohesion had been suspended by the chemical attraction exerted by another body towards it, and if this attraction suddenly cease to operate, the force of cohesion is resumed, and the solid substance appears usually in the form of a powder. This latter case forms the chemical operation of Precipitation. A similar result is obtained, when, in consequence of chemical combination, a substance is rapidly formed, between the particles of which the attraction of aggregation is exerted with considerable force.

But if the attraction of aggregation is exerted more slowly, the particles on which it operates are united not indiscriminately, but usually with regularity, so as to form masses of regular structure and figure, bounded by plane surfaces and determinate angles. This forms the operation of crystallization, and such masses are denominated Crystals.

Crystallization may take place either from a state of fluidity produced by heat, or from a similar state produced by the exertion of a chemical attraction. Of the first

we have examples in ice, which shoots in long slender crystals, when water is cooled to a sufficient extent, and also in a number of the metals which have been melted, and then subjected to slow cooling. Of the second we have examples in many saline substances, which, when they have been dissolved in water, concrete in crystals, when part of that water has been withdrawn by evaporation, or when its solvent power is diminished by a reduction of its temperature. In any of these cases, if the operation is conducted slowly, so as to admit of the particles uniting by those sides most disposed to union, crystals are formed, and these are in general larger, more transparent, and more regular in their form, the slower the crystallization has been allowed to proceed.

The production of these regular forms is favoured by affording a nucleus, from which the crystallization may commence; and still more so, if this nucleus is of the same matter as the substance to be crystallized, and is of a regular figure: and on this is founded a method of producing crystals of great regularity, and of large size.

The access of the air has likewise an influence on crystallization; a solution of a salt, for example, which has been inclosed while hot in a vessel, from which the air has been in a great measure expelled, not crystallizing when cold, but shooting into a congeries of crystals, the moment the air is admitted. The sudden admission of the air appears to operate by the pressure it exerts on the surface of the liquor, causing the approximation of the particles of the dissolved solid, whence the exertion of the attraction of cohesion is favoured; and hence any equiva-

lent pressure applied in a similar manner has the same effect.

In this sudden crystallization, is very well displayed a phenomenon, which always attends this process, the evolution of heat.

An enlargement of volume is often produced by crystallization, as in the example of ice, of several metals, and of a number of salts; while, in other cases, the reverse is the case, the volume of the crystallized substance being less than while it existed in the liquid state.

Crystals formed from a watery solution, generally retain a portion of water in a combined state. This is named their water of crystallization: when deprived of it, they lose their transparency and density. Some part with it from mere exposure to the air, and suffer these changes: they are then said to effloresce: if they attract water and become humid, they are said to deliquesce; but these properties of efflorescence and deliquescence are relative, and depend much on the state of the atmosphere with regard to humidity.

By the process of crystallization, substances may often be obtained separate which exist in the same solution. If one is less soluble than the other, it will after a certain extent of evaporation crystallize, while the other remains dissolved, and may be obtained by a subsequent evaporation: Or, if one is more soluble in hot than in cold water, while the other is nearly equally soluble in either state, the one will be obtained by crystallization when the liquor has cooled, while the other, when the necessary degree of evaporation has taken place, may separate while the solu-

tion is hot. The mutual attraction of substances dissolved together, sometimes, however, counteracts their crystallization, or causes each to crystallize with some intermixture of the other; and this, too, alters the crystalline forms which either is disposed to assume.

Crystallization sometimes takes place in the transition from the aërial form, as is well exemplified in the arrangement of a flake of snow.

Every substance in crystallizing is disposed to assume a certain regular figure; sea salt, for example, assumes the form of a cube; nitre, that of a prism. This figure, however, is not invariable, but is liable to be modified by circumstances, and the same substance is therefore found under different crystalline forms.

The theory of crystallization is still obscure. The particles of bodies may be of certain regular figures, and in uniting, these particles may be disposed to approach by certain sides in preference to others, probably by those which admit of the most extensive contact. Hence a regular structure and figure, uniform with regard to each substance, may be produced.

The mechanical structure of crystals has been investigated with much labour by Haüy. He has shewn that in every crystallized substance, whatever may be its actual form, there is a nucleus of a determinate figure, and which, by mechanical analysis, that is, by splitting the actual crystal according to its natural joinings, may be extracted. This nucleus or primitive form, he has shewn, is constant with regard to each substance, however various the actual forms of its crystals may be; and he has farther explain-

ed, how, by additions of particles to this nucleus, according to certain laws, these secondary forms may be produced. The development of this theory, however, requiring extensive details, and being not strictly elementary, I may refer for the statement of it to my System of Chemistry.

CHAP. II.

OF CHEMICAL ATTRACTION OR AFFINITY.

CHEMICAL attraction is that force by which the particles of different bodies are united intimately, forming not a mere aggregate or mixture, but a substance in which new qualities are acquired, the properties of the bodies combined being more or less changed. The term affinity has been used to denote the same power, from an opinion, that some peculiar relation or resemblance exists between those bodies, which are most disposed to exert this mutual attractive force; and the term, though derived from a groundless hypothesis, may, without any reference to its origin, be conveniently used as synonymous with chemical attraction.

The immediate result of the exertion of chemical attraction between two bodies, is the intimate union or assimilation of their particles, so as to form a homogeneous

mass. This result is in chemical language named *Combination*. It is to be distinguished from *Mixture*, in which the particles, however intimately they may be blended, still exist apart, so that they are capable of being recognised, and of being separated by mechanical operations, and retain their properties unimpaired. It is also to be distinguished from *Aggregation*, which is only the union of particles of a similar kind, forming an aggregate which has the general properties of the particles of which it is composed, whatever may be its mechanical structure or form.

The substance formed by chemical combination is named a *Compound:* the substances of which it is composed are its *Component* or *Constituent Parts* or *Principles*. When these are separated from their state of combination, the process is named *Decomposition*. If decomposition has been performed more peculiarly with the view of discovering the composition of a body, it is named *Chemical Analysis*. If the decomposed substance is reproduced by the union of its constituent parts, the operation is denominated *Chemical Synthesis*. The *Integrant particles* of a body are understood to be the most minute parts into which it can be resolved without decomposition; they are of course similar to each other, and to the substance which they form. The *Constituent particles*, again, are those into which it is resolved by decomposition, which are therefore of a different nature, both with regard to the substance itself, and with regard to each other. It is between these that chemical attraction is exerted, while

aggregation is conceived to be exerted between the integrant particles of bodies.

The theory of chemical attraction is still far from having attained perfection, though it has been the subject of much investigation. Newton, as has been already stated, suggested the idea, that the phenomena of chemical combination and decomposition might be owing to an attraction exerted between the particles of bodies, and varying in its force. This view was soon adopted by chemists. The elder Geoffroy endeavoured to ascertain the relative degrees of strength with which attraction is exerted among bodies, and gave the results under the form of a table. The subject continued to be prosecuted, until a number of observations more or less exact were accumulated, which Bergman reviewed, and placed in a clearer light. And more recently Berthollet has by his researches extended the theory of affinities, and presented views with regard to it extremely important, and very different from those which had been considered as established.

From these preliminary observations and definitions, we may proceed to the more full statement of the doctrines of chemical attraction, generalizing these as far as the present state of our knowledge admits.

Sect. I.—*Of the Phenomena which arise from the exertion of Chemical Attraction.*

The immediate result of the exertion of chemical attraction between bodies, is their intimate union or combination, and the most general phenomenon attending this combination is a change in the properties of the bodies combined. The secondary qualities of bodies, depending on the peculiar arrangements of their particles, it is easy to conceive that when these arrangements are subverted, the properties must be altered, and that in the formation of a new substance new qualities must be acquired.

Chemical combination is accordingly, in general, attended with very striking changes of properties; so striking, indeed, that we can seldom infer with certainty, from our knowledge of the properties of any body, what will be the properties of the compound it forms when united with another.

Still the entire change of properties from combination, is not an invariable result. There are many cases in which they are only modified; and in some cases, as for example in the combinations of salts with water, so slightly so, that there is scarcely any evident change, but change of form.

Berthollet has proposed a view of this subject, which in some measure reconciles these apparently opposite results.

The properties of bodies, he supposes, would always remain in their combination, but for certain causes foreign to the combination itself, by which they are modified, and in some cases entirely disguised. Thus, there are properties which are incompatible, different tastes or colours, for example, which cannot exist together, and which must therefore neutralize or modify each other. From the approximation of the particles, which is the effect of combination, changes must be produced too in the secondary qualities depending on their arrangement. The same cause must give rise to modifications of chemical properties; for if in consequence of this approximation, much cohesion is acquired, this must counteract the affinities of the principles of the compound, and of course render its action less energetic: and, on the other hand, if, by the condensation attending chemical union, the bodies uniting have passed from the aëriform state to the liquid form, this, by removing the obstacle which elasticity opposes to their chemical action, may facilitate that action, and render it more extensive and powerful. Lastly, the diminution which is produced by the reciprocal force itself that unites two bodies, in the affinities which either of them exert to others, must cause the chemical action of compounds to be in general weaker than that of their constituent principles, though this may in certain cases be modified by the other causes which operate. Thus we perceive, that notwithstanding the changes that attend combination, the theory may be just, that the properties of bodies combining, enter with them into the combination, and would always be discoverable in the compound, were it not for the opera-

tion of modifying circumstances. And we derive the rule, which in general will be found to hold true, that where energetic affinities are exerted, or where substances having opposing properties are combined, the properties will be materially changed; but where the affinity is not powerful, and therefore the combination not very intimate, or where the substances combined are such as agree in the general assemblage of their qualities, the properties of the compound will not be very remote from those of its more active ingredient, or from the mean of those of its constituent parts. Even in very intimate combinations, we can often trace the properties of compounds from those of their component parts; as, for example, the high refractive power of water, from its inflammable ingredient,—a property which led Newton to his singularly acute conjecture, that it contains an ingredient of that nature. The comparative volatility of compound salts, which are formed of principles disposed to assume the elastic form, affords a similar example.

In those combinations in which the changes of properties are least considerable, there is generally one change to be discovered to a greater or less extent, and which may even be regarded as a test of chemical union,—a change of density, the density of the compound never being the mean of the densities of its component parts. In the greater number of cases the density is augmented, and sometimes to a great extent. In other cases, however, it is diminished, or the volume is enlarged.

As in chemical combination the particles of two bodies are made to approximate, we might expect that conden-

sation would be always the result; and it is not very obvious how enlargement of volume should sometimes be produced. Berthollet has very well explained this. The immediate effect of combination is in every case condensation; but if the consequence of the combination is, that one of the bodies changes its form from the solid to the liquid, the enlargement of volume which attends this change of form may more than counterbalance the condensation from the combination; and hence, on the whole, diminution of density will be the result. It is accordingly in cases of solution, or where a solid body is acted on by a liquid, so as to be brought into the liquid state, that the exceptions to the more general law are observed. It must be added, however, that they are not altogether confined to these, but that sometimes there is enlargement of volume, even when the compound exists in the solid state, as in the combinations of some of the metals. When this happens, it is probably from a crystalline arrangement, which the particles of the solid assume in becoming solid, and is similar therefore to the increase of volume which attends the congelation of various substances.

A change of temperature, in other words the production either of heat or cold, is, next to the change of properties, the most important phenomenon attending chemical combination. The production of heat is the more frequent change: it is often intense, and the great source of heat in the operations of art is chemical combination. Cold is also, however, not unfrequently produced. It very generally is the consequence of the solution of saline substances in water, or in other more active liquids, and is

still more intense in the mutual action of salts, and snow or ice.

Wherever a production of heat is observable in chemical combination, we can trace an increased density accompanying it; and the evolution of heat may be ascribed to this, since we know, that the mechanical condensation of a compressible body produces heat. On the other hand, where cold is produced in chemical action, there is always an enlargement of volume, to which, therefore, the cold may be ascribed. But we do not find that the production either of heat or cold, from chemical action, is proportional to the increase or diminution of density. Allowing the latter, therefore, to be the cause of the change of temperature, there must be some other circumstance by which it is modified. This is the change of form. It is sufficient, at present, to state, that when a body passes from the aëriform to the liquid state, or from the liquid to the solid state, it gives out heat, and in the opposite changes absorbs it, in quantities not proportional to the degree in which the density is altered by the form; and hence such transitions of form, when they accompany chemical action, which they frequently do, modify the production of heat or cold which arise from the condensation attending the combination itself. By taking into consideration these two circumstances, the production of heat or cold from chemical action is explained with more precision than if one of them only were admitted in the theory; and there can be no doubt, that both, when they occur, have a share in producing the change of temperature.

Sect. II.—*Of the Circumstances by which the exertion of Chemical Attraction is influenced.*

Chemical attraction is not an invariable force, which, as exerted by any body, operates in all cases with the same strength. Its exertion is powerfully modified by circumstances foreign to it. Of these we can distinctly trace the influence of quantity of matter, cohesion, insolubility, specific gravity, efflorescence, elasticity, and temperature.

1. Quantity of matter. The discovery of the influence of this circumstance we owe to Berthollet. Some of the facts from which it has been inferred had been known to chemists, and in the explanations given of these some approximations made to the principle itself. By Berthollet, however, it has been more fully developed, more clearly demonstrated, and more extensively applied.

The most direct proof of the law is derived from the fact, that a compound may be decomposed if a large quantity of a substance exerting an attraction to one of its principles be made to act upon it, while from the action of a smaller quantity of the same substance no decomposition ensues. Of this there are many examples in chemistry, particularly in the decompositions of compound salts.

Another proof of it is, that a substance having an affinity to one of the principles of a compound, comparatively weaker than the affinity which they exert to each other, can still produce at least a partial decomposition of the

compound, if it be brought to act on it in large quantity; the increase in its quantity in some measure compensating for the weakness of its affinity.

Lastly, what is in strict conformity to the same law, if a compound is submitted to the action of a substance, exerting an attraction to one of its principles, even much stronger than the attraction which unites them, still the decomposition is only partial, or a portion of the principle abstracted by the decomposing substance remains combined with the ingredient with which the entire quantity of it was combined in the compound; for, in proportion as the decomposition goes on, the increase in the relative quantity of that ingredient adds so much to the force of the attraction it exerts to the principle abstracting from it, as to be able to counterbalance the attraction producing the decomposition, and therefore to suspend its action. Hence there is a partition of the substance attracted between the two bodies exerting attractions towards it; and the proportions of this partition are determined as much by the differences in the quantities of these, as by the difference of energy in their affinities.

From these general facts, which are supported by numerous individual experiments, Berthollet has established the law, that affinity is modified by quantity of matter, or, more precisely, that the chemical action of any body is exerted in the ratio of its affinity and quantity. It is one of much importance in its applications, enabling us to explain with more precision many cases of chemical combination and decomposition; and illustrating the operation

of some of the other circumstances which influence chemical attraction.

2. Cohesion. Cohesion is that force by which the integrant particles of a body are held in union: it must therefore counteract the action of any power, the tendency of which is to separate these particles, in order to bring them into new arrangements or combinations. Hence it powerfully modifies the exertion of chemical attraction; and from the opposition of these two forces, in different degrees of energy, arise numerous shades of combination, more or less intimate, as the one predominates over the other, from the mere adhesion of the surfaces of bodies, or the absorption of a liquid into the interstices of a solid, to the most perfect chemical union. If cohesion be powerful, a strong affinity may be effectually resisted, and no combination take place, though the bodies have a strong reciprocal attraction, of which we have many examples in chemistry. If cohesion be inconsiderable, a weak affinity may be predominant, and a combination be effected. And whatever diminishes the force of aggregation, favours the exertion of chemical attraction.

From the influence of this circumstance in counteracting combination, bodies in the solid state seldom act chemically on each other, whence the axiom was established in Chemistry, *Corpora non agunt nisi sint soluta.* To this there are exceptions, as in the action of various compound salts on each other, producing mutual decomposition, though both are solid, or in the action of some of these salts on ice or snow, even at very low temperatures. Yet still, in general, fluidity is necessary to chemical action; and

if not possessed by either of the bodies which are designed to act on each other, it is necessary that it should be communicated, either by the application of heat, or by the previous operation of a solvent. Hence fusion and solution are the common *media* of chemical action.

Cohesion, existing in liquids to a certain extent, may counteract their mutual attraction where this is weak; though in general the resistance it opposes is so inconsiderable, that liquids combine readily, and in all proportions.

To these views, with regard to the effect of cohesion on combination, Berthollet has added some others, more novel, and equally important. He regards it not merely as a quality of bodies actually solid (or remaining in a slight degree in liquids) resisting the exertion of affinity, and ceasing to act when solidity is destroyed; but as a force which continues to operate when it has been apparently overcome, or when its effects are not sensible, and which, by a progression in its action, may at length influence combination. It may be suspended by a superior affinity, or by the agency of heat; and its energy may be so far subdued as to appear negative; but still it continues so far active, that if the forces by which it was weakened are diminished, its action will be exerted even before solidity takes place, and will counteract affinity. Or if, in consequence of new affinities, combinations are produced, it may determine the proportions in which the elements are combined; for being exerted between the integrant particles resulting from the combination, whenever its intensity is sufficiently powerful to counterbalance the affini-

ty of the liquid in which these are formed, it will give rise to precipitation or crystallization, will of course withdraw the substance formed from the sphere of action, will oppose an obstacle to any further exertion of chemical power, and by such operation may determine the proportions of the combination. This effect, resulting from cohesion, will require to be stated more fully in considering the limits to the exertion of attraction.

3. INSOLUBILITY. This property is merely the effect of cohesion in a solid, considered in relation to the liquid in which it is exerted, and of course its operation is similar. It opposes a resistance to the exertion of any attraction towards the body possessed of it, and it is an obstacle to the progress of combination, beyond that stage at which the insolubility withdraws the substance formed from the sphere of attraction. It equally favours decomposition, when, in consequence of it, a substance, separated from a combination, is separated, and ceases to counteract the action of the decomposing substance.

4. SPECIFIC GRAVITY. Much difference of specific gravity in two bodies is an obstacle to their mutual union, since it is a cause favouring their separation, and of course a more powerful affinity is required to produce their union, than if such a difference did not exist.

5. EFFLORESCENCE. The operation of this circumstance, in influencing chemical action, is comparatively trivial, yet it sometimes can be traced. In mixtures of saline substances, a substance evolved or formed by their mutual decomposition sometimes rises on the surface in a loosely aggregated mass or congeries of minute crystals, forming

what is named an Efflorescence. It is thus withdrawn from the action of the other substances, and this may contribute to the progress of the decomposition, or allow it to become more complete. Its influence has accordingly been observed in some important cases, particularly in the decomposition of sea-salt by calcareous matter, and the production, both natural and artificial, of carbonate of soda.

6. ELASTICITY. The property of elasticity is possessed, in such a degree, as to influence chemical action only by substances in the aërial form. In that form, the particles of a body are mutually repellent; and they are thus placed at great distances from each other. When two aëriform bodies, therefore, are presented to each other, their particles are at distances too great to admit of the exertion of chemical attraction, so as to bring them into intimate union. Hence elasticity is generally an obstacle to chemical combination. In some cases where the mutual attraction is strong, it is overcome, and two aëriform bodies combine together; but more generally the reverse is the case, or the attraction does not operate.

In conformity to this view, those circumstances which repress elasticity favour the combination of elastic fluids. Mechanical pressure, strongly and suddenly applied, causes different aëriform bodies to combine. The application of cold, especially when aided by pressure, has a similar effect. What appears singular, heat often gives rise to the same result; its operation, however, which is afterwards to be considered, may be reconciled perhaps to this principle.

In the combination of an elastic fluid with a body not possessed of elasticity, as a liquid, as the obstacle to their union is in part removed, it generally takes place more readily, at least to a certain extent. Still, however, the elasticity operates, and places limits to the quantity of the aëriform body which the liquid absorbs. Hence this quantity is increased by whatever counteracts this force, as by the application of pressure. Cold has a similar effect, though the operation of this is in some measure counteracted by the cohesion it communicates to the liquid; and if this is carried so far as to produce solidity, the absorption of the aëriform body is not only counteracted, but the quantity which had been absorbed is often, at the moment of congelation, disengaged. In this way we can account for the fact, which otherwise appears anomalous, that the application of heat, especially if sudden and intense, often favours the combinations of aëriform with solid substances; the diminution which the heat occasions in the cohesion of the solid, more than counterbalancing the augmentation of elasticity in the other.

Since elasticity in general counteracts combination, it may easily be understood that it will favour decomposition. If a compound consist of a solid ingredient, and of another, which, when uncombined, exists in the aërial form, it will be less difficult of decomposition, either by the application of heat, or by the action of another substance upon it, than if it were composed of two non-elastic bodies. If exposed to heat, the elastic ingredient, being disposed to acquire the state of elasticity, its affinity to the other is weakened, and it is at length expelled. Or, if the

compound be submitted to the action of a substance which exerts an affinity to its non-elastic ingredient, this, in conformity to the usual law, weakens the affinity exerted between this and the other ingredient, and allows a portion of the latter to assume the elastic form. This again being thus withdrawn from the sphere of action, opposes no resistance to the action of the substance by which it was displaced, and therefore does not counteract the progress of the decomposition. Hence the decomposition of such compounds is in general more complete than that of those composed of inelastic substances, the substance excluded in the latter still continuing to act in opposition to the one by which it has been displaced, and the substance to which both exert an affinity remaining in combination with portions of each of them.

7. Temperature. Much of the effect of temperature, or the state of bodies with regard to heat and cold on chemical action, is to be ascribed to the operation of some of the preceding causes, and particularly to the changes which these states occasion in cohesion and elasticity. Being in general complicated, however, and giving rise to peculiar results, it requires to be considered apart.

The application of heat usually favours chemical combination, there being numerous examples where two bodies do not combine at a low temperature, but enter into combination when their temperature is raised.

When the combination of solid substances is favoured by heat, the result is obviously to be ascribed to the diminution which the heat produces in the state of cohesion, this removing an obstacle to the exertion of their mutual

affinity. Where it favours the combination of a solid with a fluid, or even with an aëriform body, as it frequently does, its operation is still similar, the cohesion of the solid being weakened, and the resistance which that cohesion opposes to the combination of its particles with those of the other substance being so far removed.

In this case, however, the result is rendered more complicated by the circumstance, that while the heat diminishes the cohesion of the one ingredient, it increases the elasticity of the other. This sometimes counteracts the combination, especially where the mutual affinity is not strong.

A very peculiar fact, and which appears at the first glance not to accord with these views, is, that heat favours the combination of elastic fluids with each other. If two bodies in the aëriform state are mingled together, it often, indeed, generally happens, that no combination takes place. But if heat be suddenly applied, as, for example, if a burning body or an ignited spark be introduced into the mixture, they instantly combine. Here the result appears altogether anomalous: the obstacle to the combination of substances in the aërial form is their elasticity, and the distances at which, in consequence of this, their particles are placed. By applying heat, this is increased, and the combination, instead of being facilitated, it might be supposed would be counteracted.

Is the following hypothesis adequate to the solution of this difficulty? When an ignited spark is introduced into the mixture, the space on which it falls has heat communicated to it, whence an expansion, proceeding from that

space, is produced; and this expansion, by the pressure it must occasion on the surrounding particles, will cause them to approximate, and thus to unite. The whole effect is instantaneous, and it is on this that it depends. Were the heat to be slowly applied, and gradually raised, it would be diffused through the whole mixture, and the particles would be merely separated to greater distances. But a single point being heated to a high degree, while the surrounding particles remain at their usual temperature, the expansion from the former must press on the latter suddenly, and more quickly than the heat can be communicated. These, therefore, instantly approximate within the space at which chemical attraction is exerted, and their union is effected. The result of the combination is a farther evolution of heat, successively but rapidly taking place, which produces a similar effect on the contiguous particles, until the combination is complete. There are some cases, however, in which so little heat is extricated, that the introduction of a single spark is insufficient, and therefore a succession of sparks must be applied.

The application of heat, in particular cases, favours decomposition as well as combination. Where, of the substances combined, one is more disposed than the other to pass into the elastic form, this tendency is favoured by a high temperature, and frequently so much so, that their mutual affinity is overcome, and decomposition ensues. By a similar operation, heat aids the decomposition of such compounds, by the affinity exerted by a third substance to the more fixed ingredient, and it often promotes the mutual decomposition of two compounds, favouring

the union of the two more volatile ingredients, and thus allowing the attraction between the ingredients, which are comparatively fixed, to operate with effect.

In all cases, then, in which heat favours chemical action, it does so by the changes it occasions in the cohesion, or in the elasticity of the bodies concerned; but these often modify each other, and hence it often gives rise to apparently opposite results; it is therefore only by considering it in relation to both, that we obtain a just theory of its operation.

The same view is to be taken of the operation of cold. By diminishing elasticity, it sometimes favours combination; and in other cases, by increasing cohesion, it may counteract this, and give rise to decomposition. Or the one of these effects may modify the other, and thus give rise to results, which, were the joint action not attended to, would appear anomalous.

From the influence of the circumstances by which chemical attraction is counteracted, the corollary follows, that it cannot be affirmed in any case that bodies have no attraction to each other. There are many examples in which bodies do not combine, as in the familiar one of oil and water; but it is obvious, that since combination is in no case the simple result of the exertion of attraction, but always of attraction prevailing over cohesion, elasticity, or specific gravity, we cannot affirm, from combination not taking place, that no mutual attraction exists. All that can be inferred is, that the attraction is not sufficiently strong to overcome the opposing forces. It is difficult to conceive

of attraction otherwise, than as a force with which every particle of matter is endowed, and which is exerted to every other; and the theory is evidently superior, which supposes this power, in particular cases, to be prevented from being efficacious, by the interference of extraneous forces, to that which supposes, that between certain substances it is altogether wanting, especially since in all cases the action of such forces can be demonstrated, at least to a certain extent, which may be sufficient to account for the result.

From the influence, too, of these circumstances, combined with the admission that all bodies have mutual attractions, it follows, as a probable conclusion, that the affinities exerted by compounds are merely the affinities of their constituent principles, modified by the circumstances under which they are exerted. It is no doubt true, that the affinities exerted by the compound are often extremely different from those of its elements: it combines with substances to which they appear to have no attraction, and it refuses to unite with others with which they form intimate combinations. But this may be expected from the very different conditions under which they operate, and it is perhaps possible to point out how they may be diversified by circumstances, the influence of which is undoubted.

Thus, from the affinity which one of the elements of a compound exerts to the other, the affinities of either to other substances must be so far counteracted, and hence the cause of what is generally the case, the attractions ex-

erted by a compound being less powerful than those of its constituent parts.

This, however, may be modified by other circumstances attending the combination, which may either concur with it, and still farther weaken the affinities of the compound, or which may counteract it, and render them even more energetic. Thus, if a substance, by combination, pass from the solid to the liquid state, it acquires the advantages derived from fluidity, and its affinities, formerly counteracted by its cohesion, may now, notwithstanding some diminution which they suffer from the combination, be exerted with more effect. Or, if elastic substances by combination form a liquid, the advantage gained from this condensation and removal of elasticity may more than counterbalance the diminution of force from combination, and may render their affinities more extensive and more powerful. Or the reverse of these modifications may happen. If the result of a combination be the transition of a substance from the liquid to the solid state, the cohesion acquired will add to the diminution of its affinity from the combination itself; or if an aëriform compound be produced, the elasticity of this may concur with the effect of the combination in weakening the energy of its action.

With these views, many facts in the details of Chemistry strictly correspond, and they afford some happy explanations of chemical phenomena. Affinities thus modified, Berthollet has named Resulting, to distinguish them from the affinities of the immediate principles of a compound, which, in contradistinction, he names Elementary. The anomalous cases of chemical attraction, which have been

placed together under the name of Disposing Affinity, appear to belong to the same class, and principally to arise from the modifications produced in elementary affinities by combination.

SECT. III.—*Of the Limits to the Exertion of Chemical Attraction.*

CHEMICAL attraction obeys certain limits; *first*, with regard to the relative quantities in which it causes bodies to combine, and, *secondly*, with regard to the number of substances between which it may be exerted, so as to bring them into simultaneous combination.

First, In the greater number of combinations, there are limits to the attraction exerted, with regard to relative quantity; or the bodies are not always combined in indefinite quantities, but often only in determinate proportions. Under this general proposition, several classes of facts may be arranged.

1*st*, There are cases in which two bodies can be combined together only in one proportion, and if an excess of either ingredient of the compound be present, it remains uncombined, with its properties unchanged. The constituent principles of water afford an example of this.

2*dly*, Attraction is frequently exerted between two bodies, as to combine them in two, in three, or even in four proportions; but these are always determinate, so that in

the intermediate proportions no combination is established. These combinations give rise to compounds which differ entirely in their properties from each other, the differences being frequently as great as if they were formed of principles altogether different. From this cause principally arise the diversities in the properties of the substances belonging either to the animal or vegetable kingdom, these consisting in general of the same principles, united only in different proportions.

3dly, Combination is sometimes unlimited to a certain extent, but when this is reached it is arrested. Water, for example, will dissolve any quantity of a salt up to a certain proportion; but when this has been combined with it, the mutual attraction ceases to operate with effect, and no larger quantity can be dissolved. The limitation of combination in this case is named Saturation; and when the water has dissolved the largest quantity of the salt which it can dissolve, it is said to be saturated with it.

Lastly, There are cases of combination absolutely unlimited, or in which bodies unite in every proportion. This is observed to happen principally in the combination of liquids with each other, where the compound retains the liquid form.

When combination takes places in determinate proportions, it generally happens that there is one proportion in which the properties of the bodies combining are mutually lost or neutralized; the distinctive properties of neither ingredient appearing in the compound; while in the proportions different from this, the properties of the ingredient which is in excess may be recognised, weakened on-

ly to a certain extent. The stage of the combination at which this happens is named the point of Neutralization, and sometimes the point of Saturation. The latter, however, is more properly employed in the sense already pointed out, as denoting the extreme of combination; and the term Neutralization is preferable, as signifying that state in which the properties of the bodies are mutually lost or neutralized.

It is a question of some interest and importance, to what causes these varieties of combination are to be ascribed; and it would be satisfactory to reduce them to one general principle. This has been attempted by Berthollet, and though, from the difficulty of the subject, some obscurity is attached to it, his views are probably just.

The principle of his theory is, that affinity is a force always disposed to operate on bodies, and to unite them in all proportions; that any limits opposed to its exertion arise from external forces, cohesion, elasticity and others, by which it is influenced, and that it is only by the operation of these that determinate proportions are established.

We find the preceding general facts in a great measure to accord with this principle. Thus, where these external forces do not operate, as in the mutual action of two liquids, the compound remaining liquid, the combination is unlimited with regard to proportion. When cohesion or elasticity is present in the subjects of the combination, as in the action of a liquid on a solid, or in the absorption of an aëriform substance by a liquid, these forces limit the quantity of the solid that can be dissolved,

or of the air that is absorbed, in the manner already explained,—the affinity producing the combination becoming weaker as the combination proceeds, while the cohesion of the remaining solid, or the elasticity of the unabsorbed air, continues as at first, and therefore an equilibrium must be arrived at, when the combination will cease. Up to that period it may take place in indeterminate proportions; but when it is reached, a limit is placed, beyond which it cannot proceed. Lastly, When, in the progress of combination, the result in any part of it is great condensation, this, by the obstacle it may oppose to the exertion of affinity, or even from the greatness of the condensation, by withdrawing the product from the sphere of action, may limit the combination to that point, or to the proportion at which this effect is greatest; or if, by particular circumstances, this is overcome, in the further progress of the combination it may again happen; and, in this way, compounds, in two or three determinate proportions, may be formed.

Precisely an opposite view has sometimes been maintained of chemical combination, that it is an attribute of the power of affinity itself to unite bodies in determinate proportions. And this principle has lately been applied with some novelty by Mr Dalton and Dr Wollaston. They proceed on the assumption, that when bodies combine chemically, they are disposed to unite in determinate proportions; and the combination is either a binary one, that is, consists of one atom or particle of the one body, combined with one of the other, or where the two bodies combine in different proportions, the combination in one

proportion is probably binary, and in the others in certain arithmetical relations, as that of two atoms with one, three with one, &c. With this principle Mr Dalton has connected a system, relating to the weights of the atoms of bodies, and has applied it to the explanation of the constitution of a number of chemical compounds.

Much of this system is hypothetical, and, with regard to the principle itself, it appears irreconcilable with the law of chemical affinity so well established, that bodies act chemically in the ratio of their affinity and quantity; for, if combination take place in determinate proportions, if one atom of *a* is disposed to combine with one atom only of *b*, what farther force can be gained from the presence of a number of particles of *b*? While, if bodies act in the ratio of their affinity and quantity, their power of combination, unless arrested by external circumstances, must be unlimited; for the action of a number of particles of the one body is, by the very supposition, held capable of being extended to one particle of the other, and there is no point at which it ceases to operate.

The question, therefore, rests on the evidence with regard to these principles. And from the numerous facts which support the conclusion, that quantity of matter influences affinity, there can remain little doubt of the truth of the principle itself, and of the superiority of the system which rests upon it. This system, too, accords better with the general train of chemical facts, than the opposite one, that chemical attraction has a tendency to unite the particles of bodies in determinate proportions.

Secondly, Chemical attraction observes certain limits, with regard to the number of substances which it combines together. It not only unites two substances; it frequently brings three or more into combination.

When three substances are placed within the sphere of chemical action, it often happens, either that two of them combine, to the exclusion of the third, or that one is combined with each of the others, being divided between them in proportions determined by their affinities and quantities. In some cases, however, instead of either of these varieties of combination, the three substances have their affinities balanced, in such a manner that they enter into simultaneous combination, and form only one compound. Even four, five, or perhaps more substances, may be thus combined together. Such combinations are named Ternary, Quaternary, &c. according to the number of their constituent parts.

There are numerous examples of such combinations among the metals. If three or four metals be fused together, they often unite, and form one uniform compound. There are also frequent examples of ternary combinations among the salts, one acid being saturated by the joint action of two bases. Nature, too, presents us with a number of such combinations. Nearly all the substances belonging to the vegetable kingdom are compounds of at least three principles; and the composition of the animal products is still more complicated, four or five principles being combined in their formation.

These combinations appear to take place principally where the mutual attractions, under given circumstances,

are nearly of the same force, and where the external forces of cohesion, &c. do not much interfere. Did the attraction of one ingredient to any of the others much exceed their mutual affinities, it would probably give rise to an insulated binary compound; or did the compound resulting from the union of any two of the ingredients differ much in its constitution from those formed by the others, this circumstance would determine the chemical action, and cause the separation of such a compound. But where neither of these circumstances is present, the affinities may be balanced, and give rise to one combination. Hence, probably, their formation more peculiarly in the vessels of vegetables and animals, where, from the motion and agitation to which they are subjected, the compression under which they are placed, and the smallness of the mass in which the affinities operate, the circumstances of cohesion and elasticity are in a great measure prevented from operating, and giving rise, as they otherwise would do, to binary combinations.

Sect. IV.—*Of the Forces with which Chemical Attraction is exerted.*

Bodies exerting attractions to others, exert them with very different degrees of force; and from this arises a series of important chemical changes.

From the attraction exerted by one substance to another, their combination takes place. But this attraction

may be inferior in force to the attraction which either of these substances exerts to a third body. In this case, if this body be brought to act on the compound which the others have formed, it will decompose it; the two which exert to each other the strongest attraction will combine, and the third will be separated. Hence arise an extensive series of decompositions; and hence, too, is derived the power of the Chemist to recover, in an insulated state, substances which have been combined together, as well as to obtain the principles of which natural compounds are formed.

The case now explained has been named Single Elective Attraction,—a substance combining with another apparently in preference to a third. It was usually supposed that this combination is exclusive, and that the substance which is displaced is obtained pure and insulated. In many cases, however, it has been discovered, that in conformity to the law of chemical attraction, that bodies act in the ratio of their affinity and quantity, the excluded substance retains a portion of the one with which it was originally combined; and in other cases it attracts a portion of the decomposing substance. It is only where the external circumstances, especially cohesion and elasticity, which influence chemical affinity, operate powerfully, that complete decomposition is produced.

When this difference in the relative forces of attraction was observed, it was a very obvious idea to construct tables in which they might be represented, as far as they were ascertained by experiment. This was first done by Geoffroy, a French chemist, in 1718, and since his time

the labours of many chemists have been directed towards correcting and extending these tables. Their construction is extremely simple. The substance whose attractions are to be enumerated, is placed at the head of a column, and the substances to which it has attractions are placed beneath it, in the order of their relative forces, the substance to which it has the strongest attraction being immediately under it, the others following in that order, and the one to which it has the weakest attraction of course closing the column. Thus the attractions of lime and of muriatic acid are represented in the following tables:

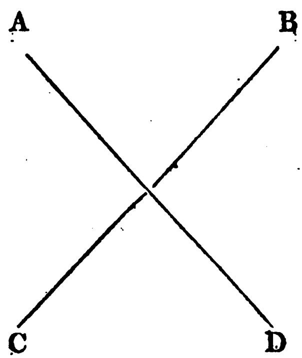
Lime.	Muriatic Acid.
Oxalic acid.	Barytes.
Sulphuric acid.	Potash.
Tartaric acid.	Soda.
Phosphoric acid.	Lime.
Nitric acid.	Ammonia.
Muriatic acid.	Magnesia.

There is another case of elective attraction, more complicated. Suppose we have a compound formed by the union of A and B, in which the force of attraction is equal to 20, and that to this compound another substance, C, is added, which has an attraction to A, equal to 16; it is evident that no decomposition can ensue. But suppose a fourth substance, D, is united to C, with an attraction equal to 7, and suppose that D has an attraction to B equal to 12, then a decomposition must be effected on mixing these two compounds; for the sum of their existing attractions is inferior to the sum of those tending to sepa-

rate them; the former, the affinity of A to B and the affinity of C to D, being equal only to 27; the latter, the affinity of C to A and of D to B, being equal to 28. A B, C, D therefore, are decomposed, and two new compounds, C A, B D, are formed.

This is what is named, in the language of Chemistry, Double Elective Attraction; two elective attractions being exerted, and two new compounds formed. Of the two attractions which are exerted, the tendency of the one is to preserve the original compounds undecomposed, that of the other is to separate their principles. The former have been named by Mr Kirwan the Quiescent, the latter, the Divellent Attractions,—terms which are generally used. It is evident, that a double decomposition can only be effected, where the sum of the divellent is superior to that of the quiescent attractions.

To represent more clearly and concisely what passes in these complicated attractions, diagrams have been constructed. The idea seems first to have occurred to Dr Cullen. The one he proposed was, that of two cylinders crossing each other at the middle.



If on mixing the compounds denoted by A C, B D, the attractions of A to B, and of C to D, overcome the quiescent attractions, A C, B D; the resulting decomposition is represented, by supposing the extremities A B, C D, of the cylinders to be brought together; by which also the production of the two new compounds will be denoted by the conjunction of these letters.

The diagram proposed by Bergman, consists of two brackets connected by straight lines, forming a square, at the sides and corners of which, the names of the existing compounds, and of their ingredients, are placed; and though not conveying a more clear idea of the operation itself, is better calculated to represent all the circumstances connected with it.

Muriate of Potash.

	Potash	32	Muriatic acid	
Sulphate of Potash.	62	▼	20=82	Muriate of Lime.
	Sulphuric acid	54 — 86	Lime	

Sulphate of Lime.

Thus in the scheme which Bergman himself gives, if the two compounds, named Sulphate of Potash, and Muriate of Lime, the former consisting of sulphuric acid and potash, the latter of muriatic acid and lime, be mixed together, a double decomposition takes place, and two new compounds, muriate of potash, and sulphate of lime, are formed. This is represented by placing on the outer sides of the two brackets the names of the two compounds mixed, and at the corners of the brackets, the names of their ingredients, so disposed that the one acid shall be diagonally opposite to the other. If the numbers expressing the relative force of attractions of the principles of these compounds be also added, it will be obvious that a decomposition will ensue. If the attraction between potash and sulphuric acid equal 62, and that between lime and muriatic acid 20, the sum of the quiescent attractions will be 82. But if the attraction between potash and muriatic acid be 32, and that between sulphuric acid and lime 54, the sum of the divellent attractions will be 86. These, therefore, will operate with effect; the muriatic acid and the potash will combine together, as will the sulphuric acid and the lime; and the names of these resulting compounds, muriate of potash and sulphate of lime, are placed without the straight lines, by which the brackets are connected.

To represent a single elective attraction, the same figure is used, with one bracket, as in this diagram.

Nitric Acid.

Nitrate of Potash. 18 A

Potash 20 Sulphuric Acid.

Sulphate of Potash.

Where the quiescent attractions are superior to the divellent, and where of course no decomposition takes place, the scheme consists of two unconnected brackets, with the names of the compounds at each side, and of their ingredients at each corner; the numbers, denoting the forces of attraction, being interposed.

In these decompositions it frequently happens, that one or both of the new compounds prove insoluble, and consequently fall down. This is denoted by bending downwards in the middle, the line placed between the substance and the square, as in diagram 2, where the undermost line is bent down to shew that the Sulphate of Lime is precipitated. If one of the substances be volatilized or sublimed, the line is bent upwards in the middle, as in diagram 3, where the upper line is drawn in this manner, to shew that the Nitric Acid is volatilized. If they are neither precipitated nor volatilized, the brackets are merely connected by straight lines.

Lastly, the circumstances under which the decomposition takes place, require to be pointed out. Sometimes it is effected by the substances being dissolved by water, sometimes by the application of heat to them in the solid state. Bergman distinguished these decompositions in the humid and in the dry way, by inserting in the middle of the diagram a triangle, △, which was the old chemical mark for fire, to denote that the decomposition was effected in the dry way, or by the application of heat; and an inverted triangle, ▽, the mark for water, to point out when it was done in a watery solution. The same method is still used, the signs only having been changed, a perpendicular line | being the mark for heat, and the compound figure, ɿ, for water. To facilitate the construction of such diagrams, all the chemical agents have likewise been distinguished by particular symbols.

Such are the doctrines of single and double elective attraction, as they were delivered by Bergman, and until lately received by chemists. A different view has been given by Berthollet of these changes, which it is necessary to explain.

In Bergman's theory, affinity is regarded as an invariable force; and the decompositions ascribed to elective attraction are considered as depending on the various degrees of intensity with which this force is exerted by each body towards others. In the theory of Berthollet, the changes are referred to the operation of those circumstances by which attraction is influenced. If the substances which in any case of complex affinity act on each other be

liquid, or be soluble in the fluid, which is the medium of action, and if the compounds they form in any stage of combination have no great cohesion or insolubility, no evident change appears when they are mixed together; there is a mutual saturation, and the opposing substances remain united, forming a combination, in which the forces are balanced. But if, on any of the parts of such a combination, the force of cohesion or insolubility, or the power of elasticity operate with energy, these external forces subvert the balance, give rise to separations, and are hence the cause of the results which were ascribed to the predominance of divellent over quiescent affinities.

Thus, if four substances are presented to each other, two of which have a greater tendency to cohesion than the others, or which form a compound of sparing solubility, instead of the whole forming one combination, the two which form the insoluble compound will, from the influence of cohesion, combine together, and be separated by precipitation or crystallization, the other two remaining in combination and in solution. And if even these four substances were previously in the reverse binary combinations, the same extraneous force will cause an exchange of principles, or the phenomena which have been ascribed to elective affinities will be produced. The case is the same where three substances are presented to each other. If the combination of two of them give rise to a substance, of sparing solubility, or having a strong tendency to cohesion, this circumstance will determine their union, and the separation of the insoluble compound, instead of the ba-

lance of affinities which would otherwise have been the result.

In other cases, the power of elasticity interferes and gives rise to similar effects, especially where heat is applied. An elastic ingredient, in what has been named Single Elective Attraction, will, from this cause, be more easily displaced; and, in double elective attractions, it will determine the combination of the two opposing substances which are most disposed to assume the elastic form.

In this theory of complex affinity, as Berthollet denominates what used to be termed Elective Attraction, there is probably much that is just; and it accords well with many facts relating to these decompositions. There is still, however, some degree of doubt with regard to the principle on which it rests; and the subject would require a discussion too abstruse to be admitted into this elementary view.

There is no problem in chemistry, the solution of which would be more important, than that with regard to the absolute forces of attractions which bodies exert. That they differ in force, as exerted by each body to a series of others, is sufficiently evident; the difficulty is to discover their degrees of strength. Were these accurately known, many of the deductions of the science would rest on calculation; but the solution has hitherto been very imperfectly obtained.

Several of the methods on which the solution has been attempted, rest on false principles. Guyton, observing that different metals adhere to the surface of quicksilver with

different degrees of force, supposed that these might indicate their respective affinities to that metal,—a method not only limited as to the possibility of its execution, but inaccurate, inasmuch as the adhesion denotes merely the facility of combination, which depends as much on the cohesion of the metals as on their attractive powers. Wenzel had supposed that the quantity of a body dissolved in a given time by another, affords a measure of the force of the affinity exerted,—a principle equally defective, since the rapidity of combination depends not merely on the affinity, but on this modified by the other circumstances which influence chemical action. Neither can any results connected with the facility of decomposition of compounds afford any certain indications, since these are equally dependent on the same circumstances.

Mr Kirwan observed a connection between the affinities of bodies and the quantities of them required to neutralize the properties of other substances with which they combine; and Berthollet, correcting and extending his views, has advanced the principle, that the power possessed by a body, of neutralizing the properties of another, is the result of the strength of its affinity to that body, and may therefore be regarded as a measure of it; the affinity of any substance to another being more powerful, as a given weight of it can neutralize a greater quantity of that other. To discover, therefore, the forces of affinity, as exerted by different bodies, it is only necessary to determine the quantities required to produce neutralization in those with which they combine.

On this principle, Berthollet has indicated the order of the affinities of the principal acids, and of the bases which they neutralize; and this order is very different from that inferred from the known series of decompositions. This, indeed, is no just objection against the theory; for these decompositions arising from the operation of other forces besides that of affinity, there are no grounds to infer that they shall correspond with the real scale of the forces of attraction. There is some reason to doubt, however, whether the principle is altogether just; and, even if it were, the investigation is, in the present state of our knowledge, attended with such difficulties, that the results are far from being certain. At the end of this chapter will be found tables representing the quantities of the principal acids and bases necessary to produce reciprocal saturation.

From the observations that have been made under this and some of the other sections, it must be apparent that the relative forces of affinity, as represented in the common tables of elective attraction, are altogether inaccurate. They represent only a series of decompositions, which arise from the operation of circumstances which influence attraction, as much as from differences in the strength of attraction itself. Nor do they even express the order of these decompositions with accuracy; since the influence of quantity, which so materially modifies the results, has been neglected. They are therefore of less utility than has been believed. As they may be condensed, however, in a short space, and may sometimes be consulted, they may be added in concluding the statement of the doctrines of chemical attraction.

TABLE OF AFFINITIES.

I.
OXYGEN.

Carbon
Zinc
Iron
Hydrogen
Manganese
Cobalt
Nickel
Lead
Tin
Phosphorus
Copper
Bismuth
Antimony
Quicksilver
Arsenic
Sulphur
Gold
Silver
Platina
Muriatic Acid

II*.
OXYGEN.

Titanium
Manganese
Zinc
Iron
Tin
Uranium
Molybdena
Tungster
Cobalt
Antimony
Nickel
Arsenic
Chrome
Bismuth
Lead
Copper
Tellurium
Platina
Mercury
Silver
Gold

III.
NITROGEN.

Oxygen
Hydrogen

IV.
HYDROGEN.

Oxygen
Sulphur
Carbon
Phosphorus
Nitrogen

V.
CARBON.

Oxygen
Iron
Hydrogen

VI.
SULPHUR.

Oxygen
Potash
Soda
Iron
Copper
Tin
Lead
Silver
Bismuth
Antimony
Quicksilver
Arsenic
Molybdena
Tellurium

VII.
SULPHURETTED HYDROGEN.

Barytes
Potash
Soda
Lime
Ammonia
Magnesia
Zircon

VIII.
AMMONIA, POTASH, AND SODA.

Acids
- Sulphuric
- Nitric
- Muriatic
- Fluoric
- Phosphoric
- Oxalic
- Tartaric
- Arsénic
- Succinic
- Citric
- Benzoic
- Acetic
- Saccho-lactic
- Boracic
- Sulphureous
- Nitrous
- Carbonic
- Prussic

* This is Vauquelin's table of the affinities of oxygen for metals, founded on the difficulty with which their oxides are decomposed by heat.

Water
Oil
Sulphur

IX.
BARYTES.

Acids
- Sulphuric
- Oxalic
- Succinic
- Fluoric
- Phosphoric
- Saccho-lactic
- Nitric
- Muriatic
- Citric
- Tartaric
- Arsénic
- Benzoic
- Acetic
- Boracic
- Sulphurous
- Nitrous
- Carbonic
- Prussic

Sulphur

X.
STRONTITES.

Acids
- Sulphuric
- Oxalic
- Tartaric
- Fluoric
- Nitric
- Muriatic
- Succinic
- Phosphoric
- Acetic
- Arsénic
- Boracic
- Carbonic

Sulphur

XI.
LIME.

Acids
- Oxalic
- Sulphuric
- Tartaric
- Succinic
- Phosphoric
- Sacchó-lactic
- Nitric
- Muriatic
- Fluoric
- Arsénic
- Citric
- Benzoic
- Acetic
- Boracic
- Sulphurous
- Nitrous
- Carbonic
- Prussic

Sulphur

XII.
MAGNESIA.

Acids
- Oxalic
- Phosphoric
- Sulphuric
- Fluoric
- Arsénic
- Saccho-lactic
- Succinic
- Nitric
- Muriatic
- Tartaric
- Citric
- Benzoic
- Acetic
- Boracic
- Sulphurous
- Carbonic
- Prussic

Sulphur

XIII.
ARGIL.

Acids
- Sulphuric
- Nitric
- Muriatic
- Fluoric
- Arsénic
- Oxalic
- Tartaric
- Phosphoric
- Acetic

XIV.
SILEX.

Fluoric Acid
Potash

XV.
ACIDS NITRIC & NITROUS.

Potash
Soda
Barytes
Strontites
Lime
Magnesia
Ammonia
Argil
MetallicOxides

XVI.
ACIDS MURIATIC & OXYMURIATIC.

The same as in NO. 15.

XVII.
SULPHURIC ACID.

Barytes
Strontites
Potash
Soda
Lime
Magnesia
Ammonia
Argil
Metallic Oxides

XVIII.
SULPHUROUS ACID.

Barytes
Strontites
Lime
Potash
Soda
Magnesia
Ammonia
Argil
Metallic Oxides

XIX.
PHOSPHORIC ACID.

Lime
Barytes
Strontites
Magnesia
Potash
Soda
Ammonia
Argil
Metallic Oxides

XX.
CARBONIC ACID.

Barytes
Strontites
Lime
Fixed Alkalies
Magnesia
Ammonia
Argil
MetallicOxides

XXI.
FLUORIC ACID.

The same as in NO. 19.

XXII.
BORACIC ACID.

The same as in NO. 19.

XXIII.
ARSENIC ACID.

Lime
Barytes
Strontites
Magnesia
Potash
Soda
Ammonia
Argil
MetallicOxides

XXIV.
OXALIC ACID.

The same as in NO. 19.

XXV.
TARTARIC ACID.

The same as in NO. 19.

XXVI.
CITRIC ACID.

Lime
Barytes
Magnesia
Potash
Soda
Ammonia
Argil
MetallicOxides

XXVII.
BENZOIC ACID.

The same as in NO. 26.

XXVIII.
SUCCINIC ACID.

The same as in NO. 26.

XXIX.
SACCHO-LACTIC ACID.

The same as in NO. 26.

XXX.
ACETIC ACID.

Barytes
Potash
Soda
Ammonia
Lime
Magnesia
Argil
MetallicOxides

XXXI.
PRUSSIC ACID.

Potash
Soda
Ammonia
Lime
Barytes
Strontites
Magnesia
Argil
MetallicOxides

XXXII.
OXIDE OF GOLD.

Æther
Acids
Muriatic
Nitric
Sulphuric
Arsénic
Fluoric
Tartaric
Phosphoric
Prussic
Fixed Alkalies
Ammonia

XXXIII.
OXIDE OF SILVER.

Acids
Muriatic
Oxalic
Sulphuric
Saccho-lactic
Phosphoric
Nitric
Arsénic
Fluoric
Tartaric
Citric
Acetic
Succinic
Prussic
Carbonic
Ammonia

XXXIV.
OXIDE OF PLATINA.

Æther
Acids
Muriatic
Nitric
Sulphuric
Arsénic
Fluoric
Tartaric
Phosphoric
Oxalic
Citric
Acetic
Succinic.

XXXV.
OXIDE OF QUICKSILVER.

Acids
Muriatic
Oxalic
Succinic
Phosphoric
Arsénic
Sulphuric
Saccho-lactic
Tartaric
Citric

Nitric
Fluoric
Acetic
Boracic
Prussic
Carbonic

XXXVI.
OXIDE OF COPPER.

Acids
- Oxalic
- Tartaric
- Muriatic
- Sulphuric
- Saccho-lactic
- Nitric
- Arsénic
- Phosphoric
- Succinic
- Fluoric
- Citric
- Acetic
- Boracic
- Prussic
- Carbonic

Fixed Alkali
Ammonia

XXXVII.
OXIDE OF IRON.

Acids
- Oxalic
- Tartaric
- Sulphuric
- Saccho-lactic
- Muriatic
- Nitric
- Phosphoric
- Arsénic
- Fluoric
- Succinic

Citric
Acetic
Boracic
Prussic
Carbonic

XXXVIII.
OXIDE OF TIN.

Acids
- Tartaric
- Muriatic
- Sulphuric
- Oxalic
- Arsénic
- Phosphoric
- Nitric
- Succinic
- Fluoric
- Saccho-lactic
- Citric
- Acetic
- Boracic
- Prussic

Fixed Alkali
Ammonia

XXXIX.
OXIDE OF LEAD.

Acids
- Sulphuric
- Saccho-lactic
- Oxalic
- Arsénic
- Tartaric
- Phosphoric
- Muriatic
- Nitric
- Fluoric
- Citric
- Acetic
- Boracic

Prussic
Carbonic
Fixed Alkali

XL.
OXIDE OF ZINC.

Acids
- Oxalic
- Sulphuric
- Muriatic
- Saccho-lactic
- Nitric
- Tartaric
- Phosphoric
- Citric
- Succinic
- Fluoric
- Arsénic
- Acetic
- Boracic
- Prussic
- Carbonic

Ammonia

XLI.
OXIDE OF NICKEL.

Acids
- Oxalic
- Muriatic
- Sulphuric
- Tartaric
- Nitric
- Phosphoric
- Fluoric
- Saccho-lactic
- Succinic
- Citric
- Acetic
- Arsénic
- Boracic
- Prussic

Carbonic
Ammonia

XLII.
OXIDE OF COBALT.

The same as in NO. 41.

XLIII.
OXIDE OF MANGANESE.

Acids
- Oxalic
- Tartaric
- Citric
- Fluoric
- Phosphoric
- Nitric
- Sulphuric
- Muriatic
- Arsénic
- Acetic

XLIV.
OXIDE OF ARSENIC.

Acids
- Muriatic
- Oxalic
- Sulphuric
- Nitric
- Tartaric
- Phosphoric
- Fluoric
- Saccho-lactic
- Succinic
- Citric
- Arsénic
- Acetic
- Prussic

Ammonia

Phosphoric
Citric
Succinic
Fluoric
Arsénic
Acetic
Boracic
Prussic
Carbonic
Sulphur

XLV. OXIDE OF BISMUTH.
Acids
Oxalic
Arsénic
Tartaric
Phosphoric
Sulphuric
Muriatic
Nitric
Fluoric
Saccho-lactic
Succinic
Citric
Acetic
Prussic
Carbonic
Ammonia

XLVI. OXIDE OF ANTIMONY.
Acids
Muriatic
Oxalic
Sulphuric
Nitric
Tartaric
Saccho-lactic

XLVII. OXIDE OF TELLURIUM.
Acids
Nitric
Sulphuric
Sulphur
Alkalis
Quicksilver

XLVIII. OXIDE OF TITANIUM.
Acids
Sulphuric
Nitric
Muriatic
Prussic

XLIX. OXIDE OF URANIUM.
Acids
Sulphuric
Muriatic
Nitric
Phosphoric
Acetic
Prussic
Carbonic
Sulphur

L. ALKOHOL.
Water
Æther
Volatile Oils
Ammonia
Fixed Alkalis
Sulphur
Muriates

LI. ÆTHER.
Alkohol
Volatile Oils
Water

LII. VOLATILE OILS.
Æther
Alkohol
Fixed Oil
Fixed Alkalies
Sulphur

LIII. FIXED OILS.
Lime
Metallic Oxides
Æther
Volatile Oil
Fixed Alkali
Volatile Alkali
Sulphur

To these tables may be added the tables of Kirwan, representing the quantities of the principal acids required to neutralize the alkalis and earths, and the quantities of these requisite to saturate the acids; the results in both, though not perhaps perfectly correct, being important both in themselves and in their relation to the question with regard to the forces of chemical affinity.

TABLE I.

100 Parts of	Potash.	Soda.	Ammonia.	Barytes.	Strontites.	Lime.	Magnesia.
Sulphuric Acid	121.48	78.32	26.05	200.	138.	70.	57.92
Nitrous Acid	117.7	73.43	40.35	178.12	116.86	55.7	47.64
Muriatic Acid	177.6	136.2	58.48	314.46	216.21	118.3	89.8
Carbonic Acid	95.1	149.6	——	354.5	231.+	122.	50.

TABLE II.

100 Parts of	Sulphuric Acid.	Nitrous Acid.	Muriatic Acid.	Carbonic Acid.
Potash	82.48	84.96	56.3	105. almost.
Soda	127.68	135.71	73.41	66.8
Ammonia	383.8	247.82	171.	Variable.
Barytes	50.	56.	31.8	282.
Strontites	72.41	85.56	46.	43.2
Lime	143.	179.5	84.488	81.81
Magnesia	172.64	210.	111.35	200.—Fourcroy.
Argil	150.9	——	——	335.—nearly, Bergman.

A table founded on the experiments of Richter is likewise of value, from the simplicity of its construction, and its extensive power of application. It consists of two columns, one composed of the acids, the other of the alkalis and earths, with numbers annexed to each, and is thus to be understood: If an article in one of the columns be taken, suppose potash in the first, to which the number 1605 belongs, the numbers affixed to the names of the substances in the other column will show how much of each of these is requisite to saturate these 1605 parts of potash: they will require, for example, 427 of fluoric acid, 577 of carbonic acid, &c. If, again, we take an article of the second column, the first will indicate, in the same manner, how much earth or alkali will be required to neutralize it. It is easy by calculation to reduce these numbers in any case to 100 parts.

Bases.		Acids.	
Argil,	525	Fluoric,	427
Magnesia,	615	Carbonic,	577
Ammonia,	672	Sebacic,	706
Lime,	793	Muriatic,	712
Soda,	859	Oxalic,	755
Strontites,	1329	Phosphoric,	979
Potash,	1605	Formic,	988
Barytes,	2222	Sulphuric,	1000
		Succinic,	1209
		Nitric,	1405
		Acetic,	1480
		Citric,	1683
		Tartareous,	1694

BOOK II.

OF REPULSION, AND THE POWERS BY WHICH IT IS PRODUCED.

THE attractions which are exerted between the minute particles of matter, are counteracted by certain forces of repulsion, and by these the arrangements and combinations to which the former give rise are modified or subverted. Their operation, therefore, is important in the production of chemical phenomena.

Of these repulsive forces, the most general in its agency is the power of Heat, or what chemists denominate Caloric. This power is present in all bodies: it is capable of being increased or diminished, and this increase and diminution are accompanied with corresponding changes in the distances at which the particles of bodies are placed. Galvanism, a principle lately discovered, likewise exerts a repulsive agency, and is even more powerful than heat in subverting chemical combination. With these agents, Light has an intimate connection. Its materiality is indeed more decidedly established, yet still it is doubtful if it exert any chemical affinities; its particles are mutually repellent, and it is not improbable, that in producing chemical changes, it operates by the repulsion it communicates to the particles of bodies.

The materiality of all these agents has been maintained. The question, however, as it relates to some of them, is far from being determined, and they are so far peculiar that their gravity cannot be ascertained; they can scarcely be procured insulated, nor can their combinations, when they enter into chemical union, be traced. They may therefore, without impropriety of arrangement, be regarded as general forces producing repulsion.

CHAP. I.

OF CALORIC.

Of the sensations we experience, none are more familiar than those of heat and cold. These are excited by bodies applied to the organs of sense, and with regard to this, no fact is more familiar, than that the same body excites at different times very different degrees of these sensations. The inference from this is obvious, that the power of producing the sensation does not strictly belong to the body applied, but depends on some principle or power which it contains, and which is capable of being increased or diminished; the increase or diminution of it in any particular substance being accompanied with corresponding changes in the power of producing these sensations. We thus arrive at the conclusion, that there exists a cause of heat,—a power or principle capable of

being communicated to bodies, and of being withdrawn from them. We can easily observe the transfer of it from one to another; for by bringing a cold body into communication with a hot one, the latter communicates to the former, to a certain extent, its power of exciting the sensation of warmth, losing at the same time proportionally the power it has of exciting the same sensation: and this communication may continue to be made over any number of bodies, until an equilibrium is established.

It is scarcely necessary to illustrate this by example. A piece of iron, which has been heated in the fire, if plunged into cold water, loses a portion of its heat, which the water acquires; the water may equally be deprived of this, and the power be transferred to another body.

So far the idea of the cause of heat is limited. It has been farther extended by the observation of other effects which it produces. When a body is heated, it is also expanded, or its volume is enlarged in every direction; when it is cooled, the volume is diminished; and the diminution or increase of volume bears a general proportion to the abstraction or addition of the peculiar power on which these effects depend.

It has, lastly, been proved, that when this expansion is carried to a certain extent, bodies change their forms, solids becoming liquid, and liquids being converted into vapours or airs.

These effects being thus connected, are justly considered as arising from the exertion of the same power. It has been distinguished by different appellations; as Fire,

Heat, the Matter of Heat, or the Igneous Fluid,—terms either ambiguous, or implying an hypothesis, and therefore superseded by the more unexceptionable appellation of Caloric.

By Caloric, then, is to be understood, a power present in bodies, the cause of their expansion, and of their conversion into the fluid and aëriform states, and which, when present in a certain quantity, excites in animals the sensation of heat, the sensation of cold being also the effect of its abstraction.

Some have considered this power as a peculiar subtle fluid diffused over matter, and capable of entering into every body; others have supposed all the phenomena exhibited by heated bodies to arise from a peculiar state of these bodies,—a vibratory motion, more or less violent, of their minute particles. The question on this subject will be more properly examined after the effects of Caloric have been considered. It is sufficient to remark, that whatever may be the nature of this power, its existence as the cause of certain effects is demonstrated; and these effects, their relations to each other, and the general laws according to which they are produced, may be investigated with sufficient precision, though the nature of the cause may be unknown.

SECT. I.—*Of the Distribution of Caloric, and the means of measuring Temperature.*

THE state of a body with regard to its power of producing the effects which arise from the operation of caloric, is termed its Temperature. In every body the temperature depends on the quantity of caloric it contains. If, at any temperature, it contain a certain quantity, the addition of caloric raises its temperature, and its abstraction equally causes a reduction of temperature.

Some estimate may be formed of the temperature from the sensation it excites, but this is extremely defective. It is necessarily very limited with regard to the range of temperature, since, beyond a certain degree, either of heat or cold, there can be no discrimination; and it is also inaccurate, from the sensations being so much influenced by various circumstances, besides the direct cause by which they are excited.

The mode, therefore, of estimating the temperature of bodies by the expansion produced by the operation of caloric, was a valuable acquisition. On this is founded the construction of the thermometer,—an instrument of the first importance in all researches on the subject of heat. Sanctorius had observed the great expansion which air undergoes when heated, and it occurred to him that this expansion might afford a measure of the variations of temperature. The instrument he used was a hollow glass

ball with a long cylindrical stem; the open end of the stem being immersed in a liquid, and part of the air expelled from the ball, the liquid of course rises in the stem, and by its ascent or descent, as it is pressed on by the expanded or contracted air in the ball, shews the alterations of volume which the air suffers from change of temperature. This instrument is liable to be affected by variations from the atmospheric pressure: from the great expansibility of air, too, it is capable of measuring only a very limited range; from this cause, however, it is extremely sensible, and is hence sometimes used to indicate minute changes of temperature. It has been rendered much more perfect by an invention of Mr Leslie, in which two air thermometers are joined together, so as to form a curved tube with a ball at each extremity, represented fig. 17.; the elasticity of the air in one ball exactly counterbalances that of the air in the other, and the column of coloured liquid between them remains in equilibrium. But when one ball receives heat, the air inclosed in it being expanded, presses more forcibly on this liquid, causes it to descend in the stem connected with this ball, and to rise in the other. This Mr Leslie has named the Differential Air Thermometer.

The thermometer was rendered much more manageable, and capable of more extensive application, by substituting a liquid as the measure of expansion, and inclosing it in a tube hermetically sealed. Spirit of wine coloured, and quicksilver, are the liquids usually employed; the latter is the most accurate, as its expansions correspond most accurately with increments of temperature, and being

less volatile, it can measure much higher temperatures; the former again has the advantage of indicating lower temperatures, as it does not congeal even at the most intense cold hitherto observed. The instrument with either is constructed by filling a glass ball, from which a cylindrical stem of a very narrow diameter issues, with the liquid, so that it shall rise partly in the stem; the open extremity is then closed. If the ball of the instrument be placed in contact with a hot body, it receives caloric, the liquid within is expanded, and rises in the stem, the rise continuing until the thermometrical liquid attain the temperature of the matter around it. When in contact with a cold body, caloric is in like manner abstracted from it; the liquid contracts and descends in the stem; and by a measured scale attached to the stem, the rise and fall, and the precise point at which the liquid stands, indicating of course its temperature, as well as the temperature of the body applied to it, are ascertained.

A difficulty was experienced in the construction of the scale, that of rendering it uniform, so that the degrees on one instrument should correspond with those on another. This was remedied by the discovery of certain fixed points in the scale of temperature always the same, and from which the scale may be formed. The points usually taken are those at which water freezes, and at which it boils. If the thermometer be immersed in freezing water, or rather in melting snow or ice, the liquid will stand at a particular part in the stem. If it be plunged in water boiling under a mean barometrical pressure, it will rise and become stationary at another part; and however these ex-

periments be diversified, the liquid will always be stationary at these points. Now, it is obvious, that the space between them may be divided into any number of degrees; and if the instrument is graduated in this manner, the degrees in every thermometer, if the same number be observed, will always be the same; and the scale also may be prolonged in each by similar degrees below the freezing point of water, so as to denote low temperatures, and above its boiling point to express higher temperatures.

The scale thus constructed being arbitrary, different forms of it have been introduced. In this country we use generally the scale of Fahrenheit, a German artist. The space between the freezing and boiling points of water he divided into 180 degrees; but instead of commencing the numeration of its degrees at the lower point, the freezing of water, he began it still lower in the scale of temperature, or at that degree of cold which is obtained from a mixture of snow or salt. The space between this and the freezing point of water, when divided into degrees, such as those between the freezing and the boiling points, gives 32 degrees; the freezing point of water, therefore, is on this scale marked 32, and the boiling point 212°.

The scale of Reaumur is rather more simple. It commences at the freezing point of water, which is therefore marked 0, or, as it is named, zero. The space between this and the boiling point of water is divided into 80 degrees; the latter therefore is marked the 80th degree. More lately a similar scale has been introduced in France, only the space between the freezing and boiling of water is divided into 100 degrees; it is hence named the Centi-

grade scale. This last is perhaps the more natural division, and hence some of the Chemists of this country have been disposed to adopt it. Fahrenheit's scale, however, arbitrary as it is in its construction, has two very important advantages: its degrees are much smaller than those of the others, and observations with it are therefore more minute; and the commencement of its numeration being low, there is seldom any necessity of expressing degrees below this: we avoid therefore the ambiguity of negative degrees. If a new scale were attempted, we might find one perhaps uniting every advantage in taking the freezing and boiling points of quicksilver, the usual thermometrical liquid, as those from which the degrees are to be numbered, dividing the space between them into 1000 degrees. The division would thus be more simple than that of Fahrenheit: the degrees would be still smaller, without being too much so for observation; the commencement of the numeration would be lower, and it would correspond nearly with the lowest natural temperature. And although the scale was constructed in relation to these points, the actual graduation of the thermometer might still be executed in the usual manner, from the freezing and boiling points of water, it being only necessary to determine carefully with what numbers on the new scale these points correspond.

Two standard points being fixed in all these scales, it is easy to establish their correspondence. Each degree of Fahrenheit's is equal to $\frac{4}{9}$ths of a degree of Reaumur's. If, therefore, the number of degrees of Fahrenheit's, either above or below the freezing point of water, be multiplied

by 4 and divided by 9, the quotient will be the corresponding number in Reaumur's scale. To bring those of Reaumur to Fahrenheit's, they must be multiplied by 9, and divided by 4. Each degree of Fahrenheit's scale is equal to $\frac{5}{9}$ths of a degree of the centigrade scale: to find the correspondence, therefore, these numbers are to be used as in the above formula.

In employing expansion as a measure of temperature, one very essential point is to be determined, before the accuracy of the method can be admitted: it is whether the expansion and contraction correspond exactly with real increments and decrements of temperature. If a thermometric liquid, from a given augmentation of temperature, say 10 degrees, expand more at one part of the scale than at another, then the indications from its changes of volume cannot be accurate. This subject has often engaged the attention of Chemists, and the result of their researches is, that the different thermometrical liquids do not expand uniformly as the temperature rises, but in an increasing ratio, or that from a given increment of temperature they suffer a greater expansion at a high than at a low part of the scale of heat. The expansions of quicksilver are most regular, and hence it gives the most accurate indications. Even these are not perfectly so, but exceed progressively, as the temperature rises, the real temperatures. To render the thermometer, therefore, perfectly accurate, the degrees on its scale ought to be accommodated to the progressive expansion; but there is still some degree of uncertainty as to the amount of the error, and from the mode in which the scale is graduated,

its extent is less important; as the two extreme points, the freezing and boiling of water, are accurately fixed, and the amount of the error, from the progressive expansion between these, is divided among the intermediate degrees. It is greatest, therefore, at the mean degree; there it is equal, according to De Luc, to 3 degrees of Fahrenheit; according to Crawford, not more than one degree.

To measure very high temperatures, other methods must be employed. An ingenious one was proposed by Newton, founded on observing the times of cooling in a body which has been at a high heat, until the temperature to which it falls can be ascertained by a thermometer, proceeding on the assumption that the times being taken in arithmetical progression, the decrements of temperature are in geometrical progression. Various methods, too, of applying the expansions of solids to this purpose, have been contrived, furnishing different pyrometers. But the mode which has been regarded as most practicable and accurate is that afforded by the pyrometer of Wedgwood. This is founded on a singular property belonging to clay, that it contracts instead of expanding by heat, the contraction remaining permanent even when the heat has been withdrawn. To apply this a gage is employed, formed of two straight rods of brass, 24 inches long, divided so as to form a scale into inches, subdivided into tenths, and fixed on a brass plate so as to converge, the distance between them being five-tenths of an inch at one extremity, and three-tenths at the other. A small cylinder of clay is framed, so as to enter the wide end of the groove, after it has been baked by a moderate heat: when

it is exposed to an intense heat, it is contracted in volume, and of course enters farther; and the degree of heat can thus be estimated by the scale. The commencement of this scale is at the point of ignition visible in day light; which corresponds, according to Mr Wedgwood's estimate, with 1077½ of Fahrenheit; and each degree of the scale he considers as equal to 130 degrees of Fahrenheit's. There is reason to doubt if this pyrometer is accurate: it is not ascertained if the contractions of the clay are equable, and any error from this source is not guarded against by the graduation being made from certain fixed points. It is useful, however, in giving certain stages of temperature, marked by peculiar effects, as by the fusion of the different metals.

Since the employment of the thermometer, or rather of the expansion of bodies as a measure of their temperature, more just and enlarged views have been acquired of the distribution of caloric. While the property of exciting the sensation of heat was the only one by which that power was characterized, it seemed a just conclusion, that those bodies which did not excite that sensation contained none of it; and this was then the philosophical, as it is still, perhaps, the popular opinion. Its fallacy, however, is easily demonstrated.

That the sensation which bodies excite is no just indication of the quantity of caloric they contain, will be apparent from considering the manner in which these sensations are excited. The temperature of the human body is generally about 96° of Fahrenheit. When any substance at a higher temperature than this is applied to our organs,

it gives caloric to the part to which it is applied, and this excites the sensation of heat: when it is of a lower temperature, it abstracts caloric, and this gives rise to the sensation of cold. Our sensations, however, are all influenced by preceding impressions. Our body is surrounded with an air, at a temperature generally inferior to the animal temperature: it is therefore always abstracting caloric. Hence it happens, that if any substance is applied to the body inferior to its temperature, but superior to the temperature of the surrounding atmosphere, the abstraction of caloric which it produces is inconsiderable, and, compared with the impression which the air makes upon us, it seems positively warm. In general, therefore, it may be affirmed, that whatever communicates caloric to our body produces the sensation of heat, and that whatever abstracts it causes the sensation of cold; but this abstraction requires to be greater than that made by the surrounding atmosphere, in order to convey to us the sensation of positive cold.

It is to be observed too, that different bodies at the same temperature occasion different sensations, according to the rapidity with which they absorb, or give out caloric. A piece of iron at 32 feels colder than a piece of wood at that temperature, because the former abstracts caloric from the hand, or whatever part of the body touches it, more rapidly than the other.

From these circumstances, it is evident, that the sensation excited by a body is no accurate measure of the caloric it contains, and that the sensation of cold will be excited by any substance whose temperature is inferior to

that of the animal body, though that substance may, and actually does contain a large quantity of caloric.

That bodies at such a low temperature contain it, is evident from the fact that their temperatures can be still farther reduced. If the thermometer be immersed in water which is freezing, the mercury will stand at 32° on Fahrenheit's scale; but even in the cold of this climate, it falls occasionally much lower. At 32°, therefore, the mercury must have contained caloric, since it is only by the abstraction of this power that it could contract in volume, and of course descend in the scale. In northern climates it has descended to 46 degrees below 0 of Fahrenheit, or 78 below the freezing point of water. At all degrees, therefore, above this, the thermometer must have contained caloric; and even at that intense cold, of which it is difficult to form a just conception, it must have contained much caloric, since, by artificial means, a further reduction of it could be effected: And if the thermometer contained caloric at these extreme colds, all bodies must have contained it, since it is the invariable property of this power to diffuse itself, till an equilibrium of temperature is established.

Even at these low temperatures there is no reason to believe that bodies were near to being deprived of their caloric, since even then their particles must have been far from being in actual contact; and it is only by the repulsive power of caloric that these particles are kept asunder. This affords a more extensive view of the distribution of this power. A solid body is to be conceived of as consisting of a number of particles of the same nature, kept

at certain distances from each other by its agency or interposition: when a portion of caloric is withdrawn, these particles approach nearer to each other; and hence the diminution of volume that takes place. But any condensation hitherto effected, is far from that in which these particles would be in contact; nor, perhaps, is such a condensation possible.

It has farther been established, that the fluid and aëriform states of bodies are owing to the presence of caloric: and therefore, as many liquids require to be exposed to the most intense cold in order to freeze them; as there are even some which have not yet been frozen; and as the greater number of the airs have not been brought even to the liquid state, it is evident that the lowest temperature which has been produced, is far distant from that point at which caloric would be totally abstracted.

SECT. II.—*Of the Effects of Caloric.*

CALORIC, by the repulsive agency it exerts, separates the particles of bodies from each other, and this operation, in progressive stages, gives rise to the three general effects of Expansion, Fluidity, and Vaporization. When a body is heated to a certain point, it becomes luminous: this state, termed Ignition, is an effect apparently unconnected with the others.

Of Expansion.

When the temperature of a body is raised, its volume is enlarged in every dimension; when the temperature is reduced, it suffers contraction; and this expansion and contraction are, under a general point of view, proportional in each body to the caloric communicated or abstracted.

The expansion from a given augmentation of temperature is very different in different bodies. Generally speaking, it is greatest in those which are most rare, and which have least cohesion; hence, it is very considerable in aëriform fluids; it is less in liquids, but still it is more considerable in these than in solids.

In attending to the results more minutely, we find it to be very different in different solids, as for example in the different metals; and in these differences, we can discover little relation between the expansibility and any physical or chemical quality. It has none to the density; and the only property with which it can be connected is the fusibility; those which are most fusible suffering the greatest expansion, though to this also there are exceptions.

In liquids, the degrees of expansion from the same augmentation of temperature are not less dissimilar, and as their expansibility is greater, these differences are even more conspicuous. In general, those liquids that are most volatile are those which are most expansible. Thus, quicksilver in the rise of temperature from 50° to 100°

of Fahrenheit, is expanded about $\frac{1}{190}$ of its original volume, water $\frac{1}{113}$, and spirit of wine $\frac{1}{33}$.

It might be expected that a similar diversity would exist in the expansions of aërial fluids. Instead of this, however, it appears to be established, that the expansions of all airs are the same, from the same augmentation of temperature. This is the result of the experiments of Dalton and Guy-Lussac; the expansion, according to the former, amounting in all of them to $\frac{1}{483}$ of the volume, for each degree of Fahrenheit; according to the latter, $\frac{1}{480}$. The apparent differences which had been observed in preceding experiments appear to have arisen from small but variable quantities of water being present, which, assuming the state of vapour, added to the volume of the aëriform fluid.

Another important fact to be illustrated with regard to expansion is, that in many bodies it is progressive with regard to temperature, or is always becoming greater as the temperature rises. Hence, from a given augmentation of temperature, the expansion is greater at a high than at a low part of the scale of heat.

This is observed particularly in liquids. Thus, dividing the scale of temperature between 32° and 212° into two equal portions, the expansion in the higher portion, or from 122° to 212°, is to that in the lower, or from 32 to 122, in quicksilver, as 15 to 14, in oil as 15 to 13, in water saturated with salt as 15 to 11.6, and in alkohol as 15 to 10.9. In all these the expansibility is progressive, though in each to a different extent. The progression

becomes always more considerable too as the temperature is higher, or rather as it approaches nearer to the boiling point of the liquid.

Since there is this increasing expansion in liquids, it might be expected that it would also be found in aërial fluids. The reverse, however, appears to be the case. The expansion was even observed by Roy and Dalton to be rather a decreasing one, or to become less as the temperature rises. This apparent result, however, might be owing to the mercurial thermometer not being perfectly accurate, but indicating augmentations of temperature in the higher part of the scale less than the real augmentations; and making allowance for this, according to the correction of De Luc, already stated, the expansions of aërial fluids will be found to be precisely equable.

These apparently anomalous facts, I have endeavoured to connect and explain by the application of the following principle: Expansion is not to be considered as the result merely of the operation of caloric, but as arising from this power, prevailing so far over the force of cohesion, which, to a certain degree, always counteracts it where it exists. And considering it under this point of view, these facts may thus be explained.

The inferior expansibility of solids compared with that of liquids, must be referred to cohesion being exerted in the former with much greater force than in the latter; and the obstacle to the expansive energy of caloric being therefore more considerable: while the great expansibility of aëriform substances is evidently owing to there being no cohesion between their particles, there is therefore no resis-

tance, and enlargement of volume is produced, limited only by the pressure under which the augmentation of temperature acts.

The difference in the expansions of different solids from the same rise of temperature, is evidently to be ascribed to the various degrees of strength with which cohesion is exerted between their particles. The same cause must be assigned for the differences in the expansions of different liquids; for although in these cohesion is weak, it still exists to a certain extent, different no doubt in each. The equability in the expansions of aërial substances, must, in conformity to this view, be ascribed to the absence of the power of cohesion: there is in all of them no resistance to the operation of caloric, and hence the expansion must be simply in proportion to the rise of temperature, and must in all be the same.

Lastly, the uniformity in the expansions of aërial substances with regard to temperature, while the expansion of liquids is progressive, must be referred to the same cause. In the former, expansion is the effect merely of the operation of caloric, and must therefore be proportional to the augmentation of temperature: in the latter, it is modified by the force of cohesion, which is exerted to a certain extent: the power of this is progressively diminished as the temperature rises; the resistance therefore to the expansive power is becoming less, and hence the expansions must become greater. It follows from this view, that in solid substances the expansibility ought likewise to be progressive with regard to temperature. The fact on this point is not well ascertained, though there are some ob-

servations which appear to prove that it is so. And as the force of cohesion is so great in solids, an elevation of temperature, even to a considerable extent, can have less effect in weakening it: hence the progression may be so inconsiderable, that in the small portion of the scale that can be accurately measured, it may not be easily ascertained.

There remain to be stated some exceptions to the law, that expansion is produced by the communication of caloric.

A striking exception is in the enlargement of volume that accompanies the transition of bodies from the liquid to the solid form. This transition is occasioned by reduction of temperature: it ought therefore to be attended with diminution of volume, or, if no difference can be discovered between the temperature of the liquid, and that of the solid formed from it, at the moment of formation, there ought at least to be no expansion. The expansion, with regard to a number of substances, is however very considerable. Water in freezing expands so much as to raise a considerable weight, or even to burst metallic vessels in which it is confined. This has been supposed to arise from the disengagement by freezing of the portion of air which water holds loosely dissolved; but it takes place when this air has previously been abstracted as much as possible, by the action of the air pump. It probably depends, according to the hypothesis suggested by Mairan, on a polarity in the particles of the water, or a disposition to unite by certain sides in preference to others. It is accordingly observed, that in freezing the spiculæ of ice shoot out at a certain angle; and in consequence of this arrangement an enlargement of volume may be produced. The same phe-

nomenon is displayed by some other substances in their congelation, though not to the same extent; as by several saline solutions, sulphur, and among the metals by iron, bismuth and antimony, and it is no doubt to be referred to a similar cause.

A very singular phenomenon, however, peculiar, as far as has been discovered, to water, is expansion, not in the actual process of congelation, but for several degrees previous to the point at which the congelation commences, and of course while perfect fluidity remains. If water be cooled in a tube adapted to render sensible its changes of volume, it contracts as the temperature is reduced, until it has fallen to about 40 of Fahrenheit's scale: it then becomes stationary, and if cooled farther it expands, and continues to expand in an increasing ratio, until it freeze. If, by avoiding agitation, the freezing be prevented at the usual temperature of 32°, and the water be cooled lower than this, the expansion still continues to proceed: it has been cooled down to 20, and even to 10, and at the last temperature it had expanded as much as it would have done had the temperature been raised to 75. The same property is displayed when the freezing point of the water has been lowered, by dissolving certain salts in it; and in this case the expansion commences at about the same distance from the point at which such a solution freezes, as it does from the usual freezing point of pure water.

This singular property of water, with regard to expansion, had been observed at an early period; and Hooke suggested that it might be merely not a real, but only an apparent anomaly, depending on the contraction of the

containing vessel. The same explanation was given by Mr Dalton. The expansion of water being in an increasing ratio with regard to temperature, the contractions it suffers in cooling must always be becoming less as the temperature falls. They become at length inferior to the contraction of the containing vessel; whence apparent expansion will take place, and for the same reason this will appear to proceed in an increasing ratio as the temperature falls. It has been found, what appears to be in conformity to this view, that the apparent expansion commences at different points of the thermometrical scale, when the experiment is made in tubes of different kinds, appearing, for example, at a higher part of the scale in a metallic tube and ball, than in one of glass, the contraction which the metal suffers from reduction of temperature being greater than that of the glass.

The reality of this property in water has been established, however, by Dr Hope, by a series of experiments executed in a manner in which this source of fallacy can have no effect. Thermometers being placed near the bottom and top of a cylindrical jar containing water, he observed, that in cooling water until it arrived at 40°, the under thermometer always indicated the lower temperature; but in cooling it below 40, the reverse took place, the thermometer at the surface indicating the lower temperature,—a decisive proof, that in cooling below this point water expands, becomes therefore lighter, and ascends. Or, in reversing the experiment, by communicating heat to water which had been cooled down to 32, the thermometer at the bottom was always higher in temperature than that to-

wards the surface; the water as it became heated contracting and falling down. This continued until the temperature rose to 38°, then the arrangement was reversed, and the warmer water above this appeared at the surface. It is obvious that these experiments are liable to no fallacy from the contraction or expansion of the containing vessel; since, whatever this be, it must have operated equally on the whole column of water, and they fully establish the existence of this peculiar anomaly in water.

Can any cause be assigned for this peculiarity? Blagden suggested, that that polarity, or peculiar exertion of the attraction of cohesion which unites the particles of water in a determinate manner in congelation, might begin to operate some degrees above the point at which the actual solidification takes place, and give rise to enlargement of volume. There is reason to believe that this even happens with regard to some other substances which expand in becoming solid. Thus, if pieces of solid iron are thrown into melted iron, they at first float, from the greater density of the iron in the liquid state; but in proportion as they melt, they sink, probably from the temperature of the liquid iron being reduced by their fusion, and from this reduction being accompanied with expansion.

One other exception to the law that bodies are expanded by the action of caloric remains to be stated; it is that exhibited by clay and the pure earth, argil, which is its base, which, when heated above ignition, contracts instead of expanding as the temperature is raised, the contraction remaining permanent when the temperature is reduced. This might be supposed to depend on the dissipation of

volatile matter; but the reverse of this is established by the circumstance, that beyond a full red heat there is no loss of weight, though the contraction continues to proceed far beyond this. It is probably owing to the exertion of the attraction of cohesion being favoured by the high temperature, in consequence of which, the particles composing the mass enter into closer aggregation; and accordingly, what is in conformity to this view, a degree of hardness is acquired, greater as the heat has been more intense. Sir James Hall observed, that a similar contraction takes place in chalk heated under compression, and this is accompanied with increase of hardness.

Of Fluidity.

When a solid substance is heated to a certain temperature, the force of cohesion between its particles is so far diminished, or is so peculiarly modified, that its parts are moved easily with regard to each other, or it passes into the fluid form. By a reduction of temperature, the particles are again united so as to be subversive of this mobility, or the body returns to the solid state. These changes of form, therefore, may be regarded as depending on the relative action of caloric, and of the force of cohesion. Were cohesion only exerted, the particles of all bodies would be closely united, and all would exist in the state of greatest density and solidity. But this is counteracted by the repulsive agency of caloric, which, when in sufficient intensity, diminishes cohesion so far as to produce fluidity.

This effect, however, does not depend merely on the

force of cohesion being weakened, but also on its action being so far modified, as to give rise to a different arrangement of the particles from that which prevails in the solid state. Cohesion remains in the fluid, and it is not easy to determine to what extent; for the mobility characteristic of fluidity may be accounted for on the supposition, that the mutual action of its particles is equal in every direction at the same distance, though a strong force of cohesion is exerted between them. And that a peculiar arrangement of the particles does take place in the transition of form, is proved by the facts, with regard to the expansion bodies suffer in becoming solid,—facts inconsistent with the supposition that fluidity depends merely on a diminution in the power of cohesion. This peculiar arrangement, however, depends on the operation of caloric separating the particles to certain distances, and allowing these modifications in their mutual actions to be established. Fluidity is therefore strictly and invariably the result of the exertion of this power, and no body can be said to be more naturally liquid or solid than another. In common language, indeed, those bodies which are liquid at moderate natural temperatures, are said to be frozen or congealed when they become solid, and those which are usually solid are said to be melted when they have been rendered liquid, implying some distinction between them. But this distinction is merely relative, and depends on the different temperatures at which, from the different degrees of force with which cohesion is exerted, these states are assumed.

Though every substance would undergo the change of fluidity from the action of heat, it often happens, with re-

gard to compound substances, that they are decomposed at a lower temperature than that which is necessary to melt them. But if this decomposition be prevented, they may be fused. This is well exemplified in the fusion of chalk or limestone, by heat applied under compression, so to prevent the dissipation of the aërial matter which enters into the composition of these substances: and in this case, the aërial ingredient seems to share its facility of being acted on by caloric with the solid ingredient, and to communicate to it greater fusibility.

Fluidity differs from expansion in the circumstance that it is not progressive, but takes place suddenly, and at a precise temperature: the solid, even at one degree lower than its melting point, having no appearance denoting approaching liquefaction; and the liquid at as small a distance from its freezing point, retaining apparently unimpaired its characteristic mobility. This, however, is not universal, there being some substances which pass through an intermediate stage of softness and viscidity, of which we can even mark numerous shades.

The process of congelation is influenced by certain circumstances besides the reduction of temperature. If agitation be avoided, a liquid may be cooled a number of degrees below the temperature at which it usually becomes solid, without congealing; water, for example, can thus be cooled easily to 28°, or 25°; it has been cooled even to 15° or 10°; but the moment it is agitated when thus cooled, congelation takes place, and the temperature rises to the usual freezing point. The kind of agitation which has this effect, is rather that which produces a vibration a-

mong the particles of the liquid than that which moves the whole mass. Another circumstance, which has an important influence on congelation, is the presence of loose particles of solid matter, and especially of the same kind of matter with that which is to be congealed: thus the introduction of the smallest particle of ice into water cooled, even a little below 32°, causes it instantly to freeze.

The influence of these circumstances is to be explained by considering congelation as a species of crystallization arising from the particles of the liquid uniting in a determinate manner. Mere reduction of temperature causes the particles of the liquid to approach in that direction least favourable to the exertion of that modified attraction by which they are to be united in the solid. Agitation, by the various motions it impresses on the particles, places some of them in that direction in which they are more disposed to unite; and a solid particle, or rather a small solid mass, affords a surface whence attraction can be exerted with more effect, and which, when it does commence, will proceed rapidly through the whole mass.

During liquefaction, a quantity of caloric is absorbed without producing elevation of temperature,—an important phenomenon more strictly connected with another part of the history of caloric, and therefore to be afterwards considered.

Of Vaporization.

The term Vaporization is applied to denote that change in which a body passes into the form of vapour or air. It s the immediate effect of the action of caloric. The ex-

pansive energy of this power separates the particles of bodies to greater distances, until the force of cohesion progressively weakened is entirely overcome, and a repulsion is established between the particles. These receding from each other, the body becomes extremely rare, and highly elastic, and thus passes into what is named the Aëriform or Gaseous State.

In general, bodies pass into this state from the liquid form, and there is often a considerable range of temperature between the two stages at which these changes of form happen. In some cases, however, solids pass into the state of vapour without becoming previously liquid, though if their vaporization be prevented by pressure they suffer liquefaction.

Elasticity, or the capability of being reduced by pressure into a smaller volume, and of expanding when that pressure is removed, is the distinguishing property of bodies existing in this state. They all possess it in a high degree. A moderate compression very sensibly reduces their volume; an abstraction of external pressure is followed by a great degree of expansion. This elasticity, too, is much increased by the farther operation of caloric; hence, very moderate changes of temperature in the aëriform fluids are accompanied with very considerable changes of volume, and under high temperatures they become mechanical agents of great power, from the elastic force they exert.

Rarity is another property characteristic of this form. The particles are separated to such distances, that the portion of gravitating matter in a given volume is compa-

ratively small. So few rays of light, too, are reflected, that no impression is made on the organ of vision; hence bodies in this state are invisible, except in the example of one or two elastic fluids, which are distinguished by peculiar colour, or where, as in the atmosphere, from the largeness of the mass, some tint of colour is displayed. The vapours in condensing lose their transparency, from the union of their particles into minute globules.

The temperature at which different bodies suffer this change of form is extremely various. Some require a temperature comparatively high, and hence usually exist in the liquid or solid state. Of these some require even an intense heat: these are named Fixed, in contradistinction to those which are more easily converted into vapour, and which are hence denominated Volatile. There are still others which pass into this form at temperatures so low, that even the greatest cold which we can apply is insufficient to condense them into the liquid form.

Substances which assume the elastic form at temperatures so low as this, being incondensible by the methods we can employ, are considered as permanently elastic. In the language of modern chemistry, they are named Airs or Gases,—these two terms, strictly speaking, being synonymous, though the term Air is also sometimes used not in a generic sense, but is applied specifically to that elastic fluid which forms the atmosphere. Substances, again, which exist in the elastic form, but which, requiring a high temperature to maintain their elasticity, can be easily condensed, are named Vapours. The state in which each exists is precisely the same, and the distinc-

tion is only relative, referring to the temperature at which it is assumed.

A different view has sometimes, however, been taken of this subject. The aëriform state has been considered as natural or essential to some bodies; and when this opinion was exploded, and the principle established, that this state uniformly depends on the action of caloric, still it was supposed that in the gases, or those possessed of permanent elasticity, the combination of caloric is more intimate than in the vapours which are more easily condensed. There are no grounds for this opinion. The difference obviously depends on the temperature at which the state is assumed. If a body require a high temperature to become elastic, it will of course remain so only while that temperature is kept up; and when this is reduced, it will return to the liquid or solid form. But, if the elastic state is assumed at a temperature lower than any natural one, or than what can be reached by artificial arrangements, the body will appear permanently elastic as it occurs in nature; and if disengaged from combinations in which it exists, it will instantly assume that state. If water, instead of requiring a temperature of 212° to convert it into vapour, suffered that change at 200° below 0 of Fahrenheit, it would always have appeared to us as a permanently elastic fluid, and perfectly analogous, so far as regards its mechanical properties, to atmospheric air.

That this property of permanent elasticity is merely relative, is well established by the condensation of several of the gases, as they have usually been considered, having

been actually effected by the application of intense cold, aided by strong pressure.

On these views is established the chemical nomenclature of the permanently elastic fluids. Being regarded as composed of solid or gravitating matter existing in this form, the generic term Gas is applied to denote the form itself, and a peculiar name is assigned to the solid base of each. Thus, there is one elastic fluid named Oxygen Gas: this phrase is applied to it as it exists in the aërial form, and the term Oxygen is appropriated to its gravitating matter. This matter cannot be obtained solid in an insulated state, owing to the peculiar relation it has to caloric, but it exists concrete in many combinations, and it is only when disengaged that it assumes the elastic form. The affinities of oxygen gas and its specific properties are of course considered as depending on this base. The same nomenclature is applied to all the permanently elastic fluids.

The transition of bodies into the state of vapour is much influenced by mechanical pressure, which, resisting expansion, counteracts that enlargement of the distance between the particles at which cohesive attraction ceases to be exerted. Hence the variations in the boiling point of liquids, according to the pressure under which heat is applied to them. Water, under the usual atmospheric pressure, boils at 212°; when that pressure is withdrawn to a great extent, it boils at 180°: if, on the contrary, it be heated under increased pressure, its temperature may be much elevated; in a metallic vessel it has been heated even to 400°, and has still remained in the liquid form. Hence too, under an entire absence of pressure, every li-

quid evaporates, the quantity being less as it is less volatile. Even quicksilver, which is one of the least volatile, there is reason to believe passes into vapour in the Torricellian vacuum.

The transition into vapour is dependent thus ultimately on temperature, but it is also much influenced by pressure; and in those cases where a high temperature is required, the change is not limited to one point, but takes place more or less considerably through a considerable range, less being formed as the temperature is low, and less too as the pressure is greater. Hence the quantity of vapour which rises from a liquid is very variable under these circumstances. Mr Dalton, from an experimental investigation, found, that the vapour rising from water, and remaining in contact with it at the temperature of 212°, sustains a column of mercury 30 inches in height, or, under these circumstances, such a quantity of vapour is formed as exerts this force: at 122°, or the mean between 212° and 32, it sustains a column equal to 3.5 inches, and at 32 it is equal to .02 inches. He farther investigated the elastic forces of the vapours from other liquids, these of course being greater as the liquid is more volatile; and from these researches he concluded, that "the force of vapour from all liquids is the same at equal distances, above or below the several temperatures at which they boil in the open air;" so that the forces being known with regard to one substance, and the temperatures at which others boil being ascertained, compared with this, the vapour formed from each, measured by its elasticity, may be discovered. More lately Mr Dalton has inferred, that

all vapours in contact with their respective liquids, if these are homogeneous, increase in elastic force in geometrical progression to the temperature; the temperature, however, being measured by a scale, divided on the principle, that the expansion of the thermometrical fluid is as the square of the temperature from its freezing point,—a conclusion of course resting altogether on the truth of this assumption.

An absorption of caloric, producing no augmentation of temperature, attends vaporization, as well as liquefaction, —an important general fact, to be afterwards considered.

From the different tendencies which bodies have to pass into vapour, we are enabled to separate them from each other when they have been combined, or when they become products of chemical action; and peculiar arrangements being requisite for this purpose, constitute several chemical operations relative to vaporization, the consideration of which, with the description of the apparatus in which they are performed, belongs to this section.

When heat is applied to recover a solid substance dissolved in a fluid, without any arrangement being made to collect the fluid, the operation, which is named Evaporation, is performed in shallow vessels, which, presenting an extensive surface, proportioned to the depth of liquor, allow it to be quickly heated, and the vapour to escape without any resistance. These vessels are of glass, earthenware, or metal, according to the nature of the substances operated on, and the degree of heat which is to be ap-

plied. In chemical experiments on a small scale, basons of glass, or of Wedgwood's earthen-ware, sometimes also of silver or platina, are used, the heat being applied by the medium of a sand-bath. In pharmacy and the arts, they are more frequently constructed of iron or lead, and the heat is directly applied.

When the object is to obtain the volatile matter by evaporation, it is carried on in close vessels, constructed so as to collect and condense the vapour. This operation is named Distillation. Different kinds of distilling apparatus are employed, adapted to different purposes.

Where the process is conducted on a large scale, as in the distillation of ardent spirits, the common still, made generally of copper, is employed. The construction of this has usually been extremely faulty. Being made of a considerable depth, proportioned to its diameter, a large body of liquor is to be heated, while comparatively a small surface is exposed to the fire, and hence a waste of heat. And the tube issuing from the head of the still, and conveying the vapour into the spiral tube placed in the refrigeratory, being generally narrow, the vapour is retarded, and by its pressure on the liquor opposes the evaporation. In this country the construction of the common still has, within these few years, received great improvements, by the skilful application of the principles which regulate distillation. The height of the still of the new construction is inconsiderable, compared with its diameter, and the tube is so wide that a free escape is allowed to the vapour; the distillation is thus performed with a rapidity which would formerly have been thought impracticable.

In the greater number of chemical operations, metallic vessels are liable to be acted on, and hence glass or earthen vessels generally require to be employed in distillation. The Retort or conical bottle, the neck of which is bent at an angle of about 60 degrees A, adapted to a receiver B, (Fig. 1. Plate I.) is the most convenient apparatus of this kind. Sometimes it is convenient to have it tubulated, as in Fig. 2. A, and to have the distance between it and the receiver increased, so that the latter may be kept sufficiently cool, by an intermediate tube or adopter B. The heat is applied to it by the medium of a water-bath or sand-bath.

In some cases of distillation, the product is not entirely a vapour, which may be condensed, but there is disengaged an elastic fluid, which is incondensible. The receiver having a bent tube issuing from it, represented by C, Fig. 2. is employed in this case; the condensible part of the product is collected in the body of the receiver, and the elastic product issuing through the tube, which terminates in a vessel of water, may be collected in an inverted bottle or jar.

In certain cases, the product designed to be obtained by distillation, is an elastic fluid, not condensible by itself, but capable of being condensed by being transmitted through water. The apparatus invented by Woolfe, Fig. 3. is employed for this purpose. It consists of a series of bottles, A, B, C, D, connected with each other by bent tubes, and connected with a retort generally by the medium of an adopter. The first bottle A is designed to collect any condensible part of the product. In the other

bottles, water is placed to nearly one-half their height, represented in the figure by the dotted line, and the tube passing from the one into the other, dips into the water of the bottle into which it is inserted. The gaseous product is thus transmitted through the water, by which its absorption is promoted; and if any portion is not absorbed by the water, it passes off by the bent tube at the end, and may be collected in an inverted jar, in a trough of water. Each of the bottles except the first has a straight tube, which rises to the height of 8, 10 or 12 inches above its insertion into the bottle, and passes so far within it as to dip in the water nearly half an inch. This tube is termed the tube of safety, and the use of it is to guard against that reflux of fluid which might happen from a partial vacuum arising from condensation in any of the bottles, the air having been expelled at the beginning of the operation, and its place supplied by vapour, which is liable to condense; the consequence of this would be, that the water being more pressed on by the atmospheric air without, than by the gas within, would pass backwards from one bottle to another, by rising through the tubes, as from D to C and from C to B, and thus the whole would be mingled together. It is prevented by the tubes of safety, as, when any such partial vacuum happens, the atmospheric air is forced through the small quantity of liquid in which they are immersed, and rising into the bottles, preserves the equilibrium.

Various improvements have been made in this apparatus. One defect in it is, that we cannot have the advantage of the immersion of the tube which comes from the

first bottle A into the liquid in the second B; for as it is designed to collect the condensible product, and ought therefore to be without water, it can have no tube of safety; and hence, if the tube issuing from it dip into the liquid in the second, whenever condensation happens, from the gas ceasing to be produced, the liquor will pass backwards into it. The contrivance that has been used to obviate this, is the tube of safety of Welther, or bent tube with an additional curvature, and a spherical ball, represented Fig. 4. as intermediate between the globular receiver A, and the common Woolfe's bottle B, and connecting them. In this is put a small quantity of water, so as to rise, when the pressure without and within is equal, about half way into the ball. If the elasticity is increased in the internal part of the apparatus, during the distillation, by the production of gas, the water is pressed upwards to the funnel at the top; if there is a condensation, it is forced by the atmospheric pressure into the ball, but whenever it has passed the curvature beneath the ball, it is obvious that a portion of air must rise through it, and will pass into the globe or bottle, to the tube of which it is adapted, and preserve the equilibrium. This tube is rather inconvenient in its form, and liable to be broken, and we can employ no great pressure with it. A simpler contrivance, not liable to these inconveniences, is, having merely a spherical ball in the long leg of the common bent tube, of such a size, that when the liquid in which the extremity of the tube dips, rises into it, this extremity will no longer be immersed, but a portion of the air will

enter. The form of this is represented in the tube which comes from the bottle B, Fig. 4.

Another imperfection which attends the common Woolfe's apparatus, is the difficulty of adapting the tubes by grinding, so that it is necessary to secure the joinings by lute. I have sought to remedy this, by having a tube fixed or soldered when the bottle is made, into that orifice into which the long leg of the tube from the preceding bottle is to enter, of such a length that it is immersed in the liquor within the bottle, and the tube which enters it having a very slight curvature at its extremity, the gas which it conveys is propelled forward, rises through the water, and passes into the next bottle; and as there is no difficulty in grinding the tubes into the bottles *from* which they issue, the whole apparatus is easily constructed without the necessity of lute. There is another form of apparatus which has likewise this advantage, in which, instead of bottles, globes are employed, from which a tube issues, straight at the neck, so that it can be fitted by grinding into the neck of the globe into which it enters, but having such a curvature, that the extremity of it dips into the liquid which this globe contains. This, which is the best of these forms of apparatus, is represented Fig. 5.

A liquid obtained by distillation is sometimes not perfectly pure, or it is dilute from the intermixture of water that has been elevated in vapour along with it. By repeating the distillation of it a second or third time, it is rendered more pure and strong: and the process is then named Rectification, or sometimes Concentration.

When the product of volatilization is a substance which condenses in the solid form, the process is named Sublimation; and as such products are in general easily condensed, a simple apparatus only is required. The alembic with its capital, Fig. 18. Pl. III. is generally used. The alembic A is merely a conical shaped vessel of glass, in which the materials are put, and exposed to heat in a sand-bath, the sublimate condensing in the upper part of it, and forming a crust on its sides. The capital B is adapted to its mouth to prevent the escape of the vapour; a small groove or channel runs in the under part, terminating in a tube projecting from it, by which any liquid is collected and prevented from running down or dropping on the sides of the alembic.

A peculiar apparatus is required for operating on aërial fluids, which remains to be described.

The Pneumatic Trough is the principal part of this apparatus. It is a trough, made of wood, lined with lead, generally of an oval form, about 6 inches deep, from 20 to 24 in length, and at the greatest breadth 15 inches; a moveable shelf being placed in it, at the depth of 2 inches from the edge, in the longest direction, so as to occupy one-half of the breadth, as is represented in Fig. 7. If a glass jar be filled with water, and placed inverted on this shelf, the trough being filled with water to the edge, it is obvious that the mouth of the inverted jar being surrounded with water, the water within it will be sustained by the pressure of the atmosphere. If, while thus filled, the extremity of a retort, disengaging gas, be placed under it, as represented Fig 6. or if another inverted jar, con-

taining any air, be turned up, under the mouth of it, advanced a little over the shelf, the elastic fluid rises through the water, displaces it, and is collected in the jar; and while tne mouth of this jar continues surrounded with water, the included air cannot escape, nor will the atmospheric air find access to it. In this way, aëriform fluids can be collected, preserved, and easily submitted to experiment. Some of them, however, are rapidly absorbed by water. These must be received and kept over quicksilver; and as this fluid is expensive, and inconvenient from its weight, a smaller trough is employed, either hollowed out of marble, or of a solid block of hard wood. This is represented Fig. 8. with an addition which is convenient,—a small rod fixed in the wooden standard on which the trough is placed, which, by a ring attached to it by a sliding arm, serves to support, without any risk, the jar filled with quicksilver, and placed on the shelf.

The other principal part of the apparatus, for operating on the gases, is the Gazometer, designed to contain gases, so that measured quantities can be withdrawn. One of the most simple forms of it, and which answers sufficiently for all common experiments, is that represented Fig. 15. It is made of tinned iron, the surfaces of which are japanned, and consists of two principal parts; a vessel A, somewhat bell-shaped, which is designed to contain the gas, and a cylindrical vessel of rather greater depth, B, in which the former is placed, and which is designed to contain the water by which the gas is confined. To diminish, however, the quantity of water, this cylindrical vessel has

a cone within it, also of japanned tinned iron, C, adapted to the shape of the gas-holder, so that this latter, when pushed down, slides between this and the cylindrical vessel, and a small quantity of water fills up the space between them. The vessel designed to contain the gas, is suspended by cords hung over pulleys, to which weights are attached, so as to counterpoise it. From a stop-cock at the under part of the apparatus, D, there runs a tube under the cylinder, which rises and passes through the cone, the opening by which it passes being soldered so as to be air-tight: it terminates by an open mouth at the upper part of the bell-shaped vessel A. This tube, at the part where it is bent at right angles, to ascend as has been described, is connected with another which also runs under the bottom, and ascends on the outside, terminating in the stop-cock E, so that from the one stop-cock to the other, through the gas-holder, there is an uninterrupted passage. When the instrument is to be used, the stop-cock E is opened, and the vessel A pressed down, a sufficient quantity of water being in the outer cylinder; the air of the vessel is forced out by the pressure, and its place is occupied by the water in which it is thus immersed. When this is effected, the stop-cock is closed, and now, if we wish to introduce any gas into the apparatus, a bent funnel, the mouth of which is placed in a vessel of water, is attached to the tube of the stop-cock D, as represented in the figure, and the stop-cock is opened. If the extremity of a retort, or of a tube conveying gas, as represented in the figure, terminate below the orifice of the funnel, the gas will rise along the tube, will ascend to the top of the

gas-holder, and this being counterpoised, will, as the gas enters, rise in the water, until it is filled, a quantity of water remaining around the mouth of it, by which the air is confined. When we wish to expel the gas, the stop-cock at D is closed, that at E is opened, a flexible tube is adapted to it, and the gas-holder being pressed down, either by the hand, or by its own weight from the removal of the counterpoising weights, a stream of gas issues from the extremity of the flexible tube, and may be transferred into a jar, or be applied to any other purpose, and its quantity may be measured by the instrument being graduated by a scale marked on the brass rod F.

The instrument connected with the gazometer in the plate, Fig. 16. is a convenient one for procuring gases from any solid substance, by the application of a strong heat. It is an iron bottle A, into which is fitted, by grinding, a tube bent at an acute angle. To this a smaller tube is adapted, the extremity of which can be adjusted to various heights, by a circular joint in the middle of it, at *b*. The bottle containing the materials from which the elastic fluid is to be disengaged, is placed in a furnace, or in a common fire, so as to be raised to a sufficient heat; the gas issues at the extremity, and may be conveyed into the gazometer, or received in an inverted jar on the shelf of the pneumatic trough. At the end of the operation, the gas ceasing to be produced, as the heat diminished, the water would be pressed into the tube, and might rise into the bottle, if the joinings were not opened. The easiest way of obviating this, is by having a small stop-cock in the

tube as at *a*, which may be opened when the production of the gas has ceased.

When a gas is extricated, in consequence of chemical action, with the application only of a moderate heat, the flask or cucurbit, with a bent tube ground to it, Fig. 19. is the most convenient.

In all accurate experiments on gases, it is of importance that the quantities should be determined with precision; and as to weigh the gases requires a very delicate and complicated apparatus, and is troublesome in the execution, chemists measure them by their volumes, and find their weights by a reference to the tables of their specific gravities which have been constructed. Hence jars graduated into cubic inches and tenths are convenient, as are also, in other cases, jars graduated into equal arbitrary parts, as represented Fig. 20. In thus estimating the weights of gases from their volumes, several circumstances require to be attended to, particularly the temperature and the pressure. Elastic fluids being so expansible, it is obvious that a considerable change in their specific gravity will be made, by a trivial alteration of temperature; the volumes therefore are always reduced to the standard temperature of 54.5, at which their specific gravities are ascertained. It is also necessary to attend to the varying pressure, whether of the atmosphere, or of any fluid in which the vessel containing the gas may be placed. The weight of the gases is fixed at the mean barometrical pressure 29.85 inches of mercury; and if the atmospheric pressure vary from this, the correction by which it is reduced to the standard is to multiply the real pressure, under

which the gas is, by the volume of the gas, divide the product by the mean barometrical pressure, and the quotient is the volume under that pressure. The effect of the pressure of the fluid surrounding the jar, is most easily obviated, by bringing it, where this can be done, to the same height without and within, or if not making the necessary correction according to its height and specific gravity.

Of Ignition.

THE effects arising from the operation of Caloric, hitherto considered,—Expansion, Fluidity and Vaporization, may be regarded as different degrees of one more general effect,—the increase which it occasions in the distances of the particles of bodies. Ignition, or Incandescence, cannot be referred to this cause, and it has apparently no connection with the others.

By Ignition is meant that illumination or emission of light, produced in bodies by exposing them to a high temperature, and which is not accompanied by any other chemical change. It is distinguished from combustion, a process in which there is also the emission of light and heat, by being the effect of the high temperature alone; while combustion is a process depending on the action of the air, of which certain substances only are susceptible, and which, when the process has ceased, cannot be renewed in the residual matter. Ignition is wholly independent of the air; all bodies, at least all solid and liquid substances, are susceptible of it; and if it has ceased from a reduction of temperature, it may be renewed by the temperature being raised.

Ignition appears to take place in all bodies at the same temperature. This is not far distant from 700° of Fahrenheit. Quicksilver boils at a temperature corresponding with 672° of Fahrenheit, and it, even when observed in the dark, does not while boiling appear luminous. Dr Irvine, from the heat which iron communicates to water, endeavoured to determine the temperature; the heat of a common fire he found to be about 790°; hence, the commencement of ignition must be between this and the boiling point of quicksilver. Wedgwood had fixed it at 947°, by measuring the expansions of silver in a pyrometrical gage: these being probably progressive with regard to temperature, would lead to the fixing it rather too high.

In the first stage of ignition, the red rays of light only are given out; as the temperature is raised there is an intermixture of others; and at the highest stage of ignition, there is the due proportion which constitutes white light. This continues undiminished as long as the temperature is kept up.

The aëriform fluids cannot be brought into a state of ignition, or rather cannot be rendered luminous, for at the due temperature their particles are probably ignited, but from their rarity a sufficient number of rays are not emitted from a given space to produce the sensation of vision. If a solid body be suspended in air at this temperature, it accordingly is soon rendered luminous.

Ignition is produced by friction and percusssion as well as by the communication of heat: a piece of glass, for example, can be rendered red hot by being pressed against a wheel of grit-stone made to revolve quickly; and the

spark struck from a flint by steel is a similar example. The ignition in these cases is probably produced by the high temperature which the attrition or percussion excites.

The theory of the production of ignition remains obscure; for it is not very obvious, how the raising the temperature of bodies should cause them to emit light. It has been supposed that the caloric is converted into light; but we have no proof of the possibility of this conversion, and, if it were possible, no cause is assigned, why it should take place at the temperature of ignition. A more probable opinion is, that the heat, by its repulsive agency, expels the light which the body contains; though with regard to this, also, there is the difficulty of accounting for the emission of light for an unlimited time. Where, however, the ignition is excited by the communication of heat, light is always communicated at the same time; where it is excited by attrition or percussion, it is not proved that the ignited state can be preserved indefinitely; and, if it were, there is the same difficulty in this case with regard to the unlimited evolution of caloric as of light. The subject will not be elucidated, until the relation between these two powers, at present so obscure, is better known.

Sect. III.—*Of the Communication and Diffusion of Caloric.*

All bodies are permeable to caloric, and its uniform tendency is to diffuse itself over matter, until an equilibrium of temperature is established. If a body, therefore, at a high temperature be placed in the neighbourhood of others at a lower, its excess of caloric passes off from it, until it arrive at the temperature of those around it; or, if a cold body is placed among others that are hot, it receives caloric until its temperature rise to an equality with theirs. This propagation of caloric takes place, even through the torricellian vacuum, and hence is evidently principally owing to its repulsive power, though, as it is also influenced by the nature of the medium in which it takes place, it depends, too, in part on some relation of the bodies which receive or part with it to this power.

This diffusion of caloric takes place in two modes. From a heated body a portion of caloric is always communicated to the matter in contact with it, and is diffused through that matter with a certain degree of celerity. But, besides this, a portion is projected from its surface in right lines with great velocity, and to considerable distances. The diffusion of caloric, therefore, must be considered under these two modes of radiation, and slow communication.

Of the Slow Communication of Caloric.

Caloric, when communicated by bodies to the matter with which they are in contact, is given out by them with different degrees of celerity, and is received by them with similar differences. There is a similar difference in the celerity with which it is diffused through them. Some, therefore, quickly assume the temperature of the surrounding bodies, and allow of this temperature being quickly established through their whole mass, while others do so much more slowly.

The property, in consequence of which, bodies thus receive caloric, allow it to be conveyed through their substance, and part with it to others, is named their Conducting power. Those which receive and part with caloric quickly, are those also through which it is diffused most speedily; and they are considered as better conductors than those in which the same effects are more slowly produced. In this property there are great differences, there being scarcely two bodies from or through which caloric is communicated with equal facility.

This property can scarcely be connected with any of the physical qualities of bodies. There is, indeed, a general relation between it and their density; those which are dense, as the metals, being the best conductors; and those which have much rarity conducting much less perfectly. But in examining more minutely the degrees of conducting power, we do not find that they are proportional to the densities, even among those bodies which have a similar nature, as among the different metals. In sub-

stances which are very porous, and in the interstices of which a quantity of air is lodged, the conducting power is very imperfect, which appears to be owing principally to the air being a bad conductor, and to its motion, by which it might distribute caloric more quickly, being impeded by the force with which it is retained.

It is to this cause, that the imperfect conducting power of fur, flannel, and other similar substances is owing, and on this depends their utility as articles of clothing, in preventing the abstraction of warmth.

To this difference, too, in conducting power, is owing the difference in the sensation either of heat or cold, excited by different bodies applied to our organs of sense, when the thermometer shews their temperature the same. Those which part with caloric most readily will be those which, when applied hot, will give the greatest sensation of heat; and the same bodies, being those which receive caloric most readily, will be those which, when cold, will abstract it most rapidly, and will therefore produce in greatest intensity the sensation of cold.

Many useful applications are made of this difference in conducting power, as in the various arrangements to prevent the waste of heat in chemical operations, or to guard against the effects which arise from sudden alterations of temperature.

The communication of temperature through liquids, is much accelerated by their mobility; the portion directly receiving heat having its density diminished, unless it occupy the surface changes its place; it is succeeded by another portion heated in its turn, and thus a circulation is

established through the whole mass of liquid, by which the increased temperature is much sooner established than it would be, were the caloric communicated, as in solids, merely from one particle to another.

Rumford, from some observations on the rapidity of the currents in a liquid heating or cooling, and on the slowness with which a liquid is heated or cooled when these are prevented, advanced the opinion, that it is by these motions that the uniformity of temperature in a liquid is established, and that liquids in themselves are non-conductors of caloric, or are incapable of communicating it from one particle to another. In support of this opinion, he brought forward a series of experiments designed to prove more distinctly, that when the motions of a mass of fluid are impeded, the transmission of caloric is extremely slow. He also endeavoured to establish, what would have demonstrated the truth of his opinion, that increased temperature cannot be communicated from the surface of a liquid, downwards to the rest of the mass. But, in all his experiments, the results are either inconclusive, or require so many assumptions to render them otherwise, that the opinion remained extremely problematical. The principal fact from which the question can be decided, that relating to the communication of temperature through a fluid from its upper surface, has been made the subject of experiment by various chemists, and in all of these the communication has been proved to take place. There is one source of fallacy, indeed, attending the experiment, from the conducting power of the vessel containing the liquid which may convey a portion of caloric, and com-

municate it to the under portions of the liquid. But, when this is guarded against by various arrangements, or still more effectually by making the experiment at the temperature of 32°, and in a vessel of ice, which not being capable of having its temperature raised above that point, is of course incapable of communicating any higher temperature, still the same general result is obtained, a result which sufficiently establishes the conducting power of liquids.

This conducting power, there is reason to believe, however, is not very considerable, since from the very mobility of a liquid, a particle of it, when heated, recedes from the others, and yields the caloric it had received less readily; and hence caloric is diffused through liquids, principally by the motions produced by the changes of density they suffer from changes of temperature. Still we can discover in liquids different degrees of conducting power: thus, quicksilver takes the temperature of any body with which it is in contact, and admits of this temperature being uniformly established through its mass, much more quickly than water or alkohol;—a difference which cannot be ascribed to its being more expansible or more mobile, for neither of these is the fact, and which must therefore be referred to superior conducting power,—a superiority in conformity to the general fact, that metals conduct caloric better than other substances.

A similar opinion was advanced with regard to aërial fluids,—that they also are non-conductors. It rested on observations and experiments still less conclusive than those adduced to establish the non-conducting power

of liquids; and the same conclusion that they are only imperfect conductors, is probably to be drawn with regard to them. We can even observe differences in the conducting power of different gases. Thus humid air conducts caloric better than dry air, and hence the greater sensation of cold we experience from it when at a low temperature. Mr Leslie has found, too, that bodies cool with different degrees of celerity in different elastic fluids, which he infers is owing to these having different conducting powers.

It is by the movements of fluids elastic and non-elastic, that caloric is distributed with more uniformity in nature, and that the temperature of the globe is preserved more equable than it otherwise would be. The atmosphere, when heated at the earth's surface, is expanded, becomes lighter, and recedes from it to the upper regions. An ascending current is thus formed, wherever the earth is much heated, which is replaced by cold air flowing at the surface, and this prevents that progressive augmentation of temperature which would otherwise happen. The warm air is, from the constant ascending current, propelled to colder regions, where it yields its excess of heat. A similar agency, though to a less extent, is exerted by the water of the ocean. When cooled at the surface, it becomes heavier and descends; and, from its saline impregnation, this continues to take place to a lower temperature than if it were fresh. A portion of warmer water of course ascends, and from the great depth of the ocean this circulation continues, communicating warmth, and the water at the surface does not freeze, except in latitudes where the most

intense cold prevails. From these movements it is not improbable that there is a general circulation in the ocean, as there is in the atmosphere; the water which has descended in colder regions spreading on the bottom of the sea, flows towards the equator, which must produce a current at the surface in an opposite direction, and thus the heat of the torrid zone may be moderated, as well as the cold of the polar circle.

Of the Radiation of Caloric.

Besides the caloric, which a body in cooling communicates to the matter with which it is in contact, a portion is thrown from its surface in right lines, moving with great velocity, capable of being rendered sensible at a considerable distance, and obeying the same laws of motion as the rays of light. This forms the radiation of caloric. It was observed more than a century ago, by Mariotte, and also by Lambert; and within a later period, it has been investigated by Scheele, Saussure, and Pictet, Herschel, and Leslie.

The experiment in which this radiation of caloric is best displayed, consists in placing a hot body, as a heated ball of iron, in the focus of a concave metallic mirror, opposite to which, at the distance of 10 or 12 feet, is placed a similar mirror, having the ball of an air thermometer in its focus *. The moment the hot body is introduced, the op-

* The differential air thermometer is well adapted to shew these effects, and to allow all the facts with regard to the radiation of caloric to be determined with much accuracy. It was applied to this purpose by Mr Leslie.

posite thermometer indicates elevation of temperature, the air in its ball being expanded, and pressing on the liquid so as to cause it to descend. If the hot body be withdrawn, or a skreen be interposed between the mirrors, the temperature falls, and the liquid in the thermometer rises to its former height. In this experiment, there has been projected a calorific matter from the heated body, on the surface of the mirror in the focus of which it is placed; this has been reflected in right lines from the surface of this mirror to the one opposed to it, it is again reflected from the surface of that mirror, and is collected in its focus where it produces a heating effect.

The effect is similar with a single mirror. If a hot body be placed before its concave surface, at the distance of a few feet, and a thermometer be placed in its focus, rays of caloric are projected from the hot body, and are reflected from the surface of the mirror on the thermometer, producing elevation of temperature.

That it is not the contiguity of the hot body to the thermometer that produces the effect in these experiments, is well shewn, not only by the distance at which it happens, but also by moving the thermometer a little out of the focus, even nigher to the heated surface, when its temperature, if it had been previously raised, immediately falls.

The rise of temperature produced by this radiation is greater, the hotter the body is from which it takes place. In using the apparatus of the double mirrors, and placing in the focus of one of them a ball of iron, two inches in diameter, at an obscure red heat, the elevation produced

in a thermometer, in the focus of the other mirror, at the distance of 12 feet, is equal to about 20 degrees of Fahrenheit's scale. From a glass matrass, containing about two ounces of water boiling, it does not exceed three degrees. From burning charcoal, the heat is such, that it can set fire to a burning body at the distance of several feet.

The velocity with which radiant caloric moves, is not capable of being measured at any distance at which we can make the experiment. In an experiment by Pictet, the effect appeared instantaneous at the distance of 69 feet. It appears to pass through the atmosphere without interruption; nor, according to Scheele's experiments, is its direction changed by a current of air. It is stopped, however, by liquids, even the most transparent.

Glass also intercepts a large portion of it. If a plate of clear glass be interposed half way between the two mirrors, a hot body being in the focus of the one, and the ball of a thermometer in the focus of the other, the effect on the thermometer is nearly entirely intercepted. The rays of caloric thrown on the glass, instead of passing through it, are absorbed by it. This result affords a method of separating the rays of caloric from the rays of light, when they accompany each other. Thus, if a burning candle be placed in the focus of the mirror, and a plate of glass interposed, a luminous image is formed on the ball of the thermometer in the opposite focus, from the light passing through the glass, but the calorific effect is greatly diminished, by the rays of caloric being arrest-

ed,—a fact which shews well the essential difference between radiant caloric and light.

Some bodies are more disposed to absorb radiant caloric than others, and hence are much more heated by it. Scheele observed, that when a glass mirror is used instead of a metallic one, the heat is not reflected, but is absorbed and retained by the glass; and the result is similar, if a metallic mirror have its surface blackened. Pictet found, that when the glass bulb of the thermometer is blackened, it is considerably more heated than when it is clean. But if the bulb be covered with tinfoil, the reverse happens, or the elevation of temperature is much less than when the glass bulb is opposed to the mirror.

The power of reflecting the rays of caloric is of course the reverse of the absorbing power. Metals reflect most perfectly, hence the calorific effect is greatest in these experiments when metallic mirrors are employed; it is less with a glass mirror, and is scarcely sensible when the surface is blackened. It is, for the same reason, least when the ball of the thermometer has a metallic surface, is greater when of glass, and still greater when blackened.

An important difference exists among bodies in the power of radiating caloric, the quantity thrown from different kinds of surfaces at the same temperature being very different. For the knowledge of this, we are indebted to Mr Leslie. The apparatus he employed to determine it is very simple. It is a canister of tinned iron in the form of a cube, the side being six or eight inches square; this is filled with hot water, a thermometer being

inserted in it, to shew the temperature during the continuance of the experiment. The sides of the canister are variously prepared; one, for example, is blackened, another is covered with paper, a third has a plate of glass applied to it, and the fourth is left clean. When thus prepared, it is placed before the concave surface of a mirror of tinned iron, at the distance of three or four feet; the ball of the differential thermometer being adjusted to the focus. All these surfaces being equally under the influence of the hot water in the canister, are at the same temperature, and their comparative powers, in radiating caloric at a given temperature, can be ascertained. In this respect they differ widely; as an average it may be stated, that the calorific effect from the blackened surface being 100, that from the paper is 98, from the glass 90, and from the clean metal not more than 12.

It thus appears, that those surfaces most disposed to absorb radiant caloric, when it is thrown upon them, are those likewise most disposed to radiate it when they are at a high temperature, and the absorbing and radiating property are opposed to the reflecting power.

It is an interesting question on this subject, does radiant caloric suffer refraction? This was attempted to be determined by Pictet, but the experiment was so imperfectly performed, that no conclusion could be drawn from it. Herschel found reason to conclude, that rays of caloric exist in the solar beam, apart from the rays of light, and that these are separated when the beam is decomposed, by being passed through the prism, the calorific rays being thrown beyond the red ray; this, if the experi-

ment were accurate, proved, that these calorific solar rays at least are subject to refraction. He farther submitted to experiment, the radiant caloric projected from heated bodies; and he found them to be refracted by a lens, and in the spot where they were collected by the refraction, to produce a heating effect.

Mr Leslie observed, that a considerable aberration happens in the reflection of heat; hence, when reflected from a mirror, the maximum of heat is not in the true focus, but is found to be considerably nearer to the surface of the mirror.

If the experiments of Herschel be admitted as accurate, they establish the important discovery, that radiant caloric exists in the rays from the sun, and that on this depends their heating power. In decomposing the solar beam by transmission through a triangular glass prism, it is resolved into different coloured rays, and these Herschel found were possessed of different degrees of heating power, the violet ray, which is the most refrangible, and which bounds the coloured spectrum on one side, being least powerful in exciting heat; and the calorific power, increasing towards the other side, bounded by the red ray, which far exceeds the others in heating power.

All this, however, might be considered as arising from a diversity of heating power in the visible rays of light; but Herschel farther found, that calorific rays which produce no illumination exist in the solar beam, which being less refrangible than any of the rays of light, occupy a space beyond the red ray, when the entire beam is decomposed by the prism. In this space, to the extent even of

half an inch beyond the visible light, the heating power is actually greater than in the space occupied by the red ray, which of any of the coloured rays produces the greatest heat, and it can be traced even to the extent of an inch and a half. This appears to prove the existence of rays of caloric in the solar ray, which, from being less refrangible, are capable of being separated from the visible light, and if the accuracy of the experiments be admitted, scarcely any other conclusion can be drawn. Herschel farther infers, that the heating power of the different coloured rays does not belong to the light of these rays, but depends on rays of caloric associated with them, there being, according to his hypothesis, rays of caloric as well as of light of different degrees of refrangibility, and the former being therefore spread over the space occupied by the prismatic spectrum as well as the latter. This being more intimately connected with the chemical history of Light, will be afterwards more fully considered. In one respect the calorific rays in the solar beam differ from those projected from heated bodies; they pass without interruption through transparent media: this is evident indeed from the intense heat produced in the focus of a lens when the rays of the sun have been transmitted through it. It was ascertained, too, with more accuracy by Herschel, the solar calorific rays, whether associated with light or separated from it, passing through transparent substances and producing heat; while the radiant caloric from heated bodies is almost entirely arrested.

An important subject of inquiry is still to be consider-

ed; What is the nature of Radiant Caloric, or what theory can be given of the phenomena it displays?

These phenomena appeared to prove the existence of a subtle calorific matter, projected from heated bodies, capable of moving in right lines with velocity, and obeying laws of motion similar to those of light; and this conclusion was accordingly generally drawn and received. Mr Leslie, however, advanced a different hypothesis; the apparent calorific emanation he supposed to be propagated entirely by the medium of the air. The heated surface, according to his view, communicates increased temperature to the portion of air in contact with it, this layer of air is expanded, and presses on the portion immediately before it. This is successively, but rapidly renewed; a chain of undulations is propagated from the heated surface to the mirror, reflected and concentrated in its focus, and each pulsation being accompanied, according to the hypothesis, with a discharge of the caloric by which the expansion exciting it had been produced; the whole is transported with the velocity of these undulations, and the calorific effect is obtained where they are concentrated on a solid substance. The degree of heat excited will, of course, be greater as the temperature of the surface communicating it is greater. And the diversity in the effect from different kinds of surface at the same temperature, Mr Leslie explains by the hypothesis, that they admit of a more or less perfect contact of the atmospheric air; those with which the air comes into closest contact, and this, of course, is supposed to be the case with the blackened surface, communicating the largest quantity of

caloric in a given time; and for a similar reason, the same surfaces will be those most disposed to receive caloric, and will therefore be those most heated by this kind of communication.

This hypothesis rests principally on certain facts observed by Mr Leslie with regard to the effect of skreens interposed between the hot body and the mirror on the calorific radiation. It had been observed, that when a plate of glass is interposed, the effect on the thermometer in the focus is greatly diminished. Mr Leslie found that this is much dependent on the distance at which the glass plate is placed from the heated body. In the apparatus with the single reflecting mirror, if the plate of glass be placed at about two inches from the blackened surface of the canister, a rise in the thermometer is produced equal to about one-fifth of what would be produced by the same surface, the glass being withdrawn; if farther removed from the heated surface, the effect on the thermometer diminishes, and when it is removed about a foot, it does not amount to one-thirtieth of what it is in the first position. Mr Leslie farther found that the effect was very different with skreens of different kinds; with one of paper interposed, it did not differ much from that with the glass, but if a metallic skreen was used, though extremely thin, as for example gold leaf, the effect on the thermometer was completely intercepted.

These results cannot be explained on the supposition that these skreens operate by intercepting more or less the calorific radiation, some doing so completely, others more imperfectly; for, were this the case, the action of

those which allow a certain degree of heating effect to be produced on the thermometer ought to be the same at whatever distance it is placed from the heated surface, while the fact is, that it is much dependent on its contiguity to it. They therefore, Mr Leslie conceives, establish the conclusion, that these skreens, in every case, arrest the radiant caloric, and that where any effect is produced on the thermometer, this is to be ascribed to the interposed skreen acquiring heat, and being thus enabled to display the same action as a similar radiating surface would do at the same temperature. Accordingly, when a skreen is employed which is not much disposed to receive radiant caloric on the one hand, or to radiate it on the other, as one of metal, no effect is produced; or if the skreen is such, that its temperature cannot be raised, as is the case for example with a plate of ice, there is also no effect; but, if the skreen be of a substance disposed both to absorb and radiate caloric, as in the case with glass or paper, then a certain effect will be produced, the side next to the hot body arresting the calorific radiation and having its temperature raised, and the other radiating proportional to this rise of temperature, — and this, of course, will be greater the nigher the skreen is to the heated body.

Now this effect of these interposed skreens, Mr Leslie farther conceives, can only be explained on the supposition that the air is the vehicle of the communication as already explained, the skreen arresting the chain of pulsations, and acquiring in its turn to a certain extent the power of transmitting these pulsations with the accompany-

ing discharges of caloric from the other surface; and on this assumption in a great measure rests his hypothesis.

It is one which does not appear necessarily to follow, and it is perhaps equally conceivable on the hypothesis of the existence of rays of caloric, that these may be arrested by the skreen, its temperature may be raised, and corresponding rays be projected to a certain extent from its other surface: it must, in fact, be supposed, that the interposed skreen receives caloric at the one surface, and communicates it from the other, whether the caloric be supposed to be propagated by pulsations in the atmosphere, or by actual projection of calorific particles; and in either hypothesis, those most disposed to receive it, and again to discharge it, will be those which will admit of the greatest heating effect being produced on the thermometer.

There is also some obscurity with regard to the principle of Mr Leslie's theory; for admitting, that a chain of vibrations, such as he supposes, may be established in an elastic medium from a heated surface, it is not very obvious how each pulsation should be accompanied with a discharge of the heat by which it had been excited. Or if there is any necessary connection between these events there remains the difficulty of accounting for the slow communication of caloric through elastic fluids. The theory, too, is incompatible with the results of the experiments of Herschel and Englefield; which, if they are admitted as accurate, establish the existence of a subtle calorific matter, capable of rapid projectile motion. These experiments, however, Mr Leslie considers as altogether fallacious.

It has sometimes been conceived that radiant caloric is

a species of light. Dr Hutton, assuming that the heating powers of the different species of visible light are not proportional to their power of exciting vision, supposed there might be a species of light capable of exciting temperature without exciting this sensation, and such he conceived to be the nature of radiant caloric. There appears little foundation for this hypothesis. So far as we can trace, radiant caloric has all the properties of caloric conveyed by slow communication, and the mere circumstance of its assuming a state of projectile motion, if it actually do so, is insufficient to identify it with light. It exerts none of the chemical agencies of light. And the very basis of the hypothesis is subverted; for, as is afterwards to be stated, it is uncertain if any of the rays of light apart from caloric have a heating power.

It is an interesting object of investigation, what is the relation subsisting between those two modes in which caloric is discharged from bodies, that by radiation, and that by slow communication? There appears, in general, reason to infer, that those which at a given temperature give off most caloric by communication, discharge least by radiation, and *vice versa*,—metals, for example, radiating imperfectly, while they yield caloric readily by communication, while glass is, with regard to these properties, precisely the reverse.

An inquiry of equal importance is, what proportion does the caloric discharged by radiation from a body suffering

reduction of temperature, bear to that given out by slow communication? The influence of each of these modes is established by numerous facts. That of slow communication is well shewn by the different degrees of celerity with which a body cools, according to the conducting power of the medium with which it is in contact, or according as the conducting power is favoured by frequent renewal of that medium, as, for example, by the application of a current of air, or agitation in a liquid. The influence of radiation is not less important, and has, in particular, been very clearly established by some very excellent experiments by Mr Leslie on the celerity of cooling in vessels, which radiate caloric unequally; water, for example, cooling more quickly in a tin vessel coated with lamp-black than when clean, the coating, though diminishing the conducting power, more than compensating for this by increasing the radiating power.

The proportion between the two must be considerably dependent on the temperature at which the estimate is made; for at high temperatures the cooling by slow communication will be accelerated by the more rapid current formed in the surrounding medium from the heated surface, while this can have no effect on the radiation. Mr Leslie concludes from his experiments, that at low temperatures the heat lost by the direct communication is somewhat less, and at higher temperatures considerably greater than what is lost by radiation.

The influence of these circumstances on refrigeration gives rise to some results rather singular, and to some practical applications of considerable importance. Thus

water cools more quickly in a metallic vessel, the outside of which is blackened, coated with varnish, or even covered with linen, than when clean and polished. Hence, in conducting the process of artificial refrigeration, vessels with such coatings will allow it to be performed most quickly; for the same reason, where the object is to condense vapour or steam, as, for example, in applying this condensation to procure heat, the external surface of the tubes through which the steam passes ought to be painted or blackened; while, if it is of importance to prevent as much as possible the condensation, as in conveying steam, or applying its elasticity as a mechanical power, the external surface ought to be clean and bright.

THE law observed by a body in cooling, in whatever mode the caloric be given out from it, whether by radiation or communication, has been frequently a subject of investigation. The higher the temperature is, a larger quantity of caloric is given out in a given time, and, of course, the nearer a heated body approaches to the temperature of the surrounding medium, smaller portions are evolved. Newton supposed that the progression is geometrical, taking the times in arithmetical progression, and this law appeared to be established by the experiments of Kraft and Richman. Martine, on the contrary, inferred that the decrements of temperature in a body cooling are partly equable, and partly in proportion to the subsisting heats; and Mr Leslie has drawn the conclusion from his

experiments, that the rate of cooling follows a higher ratio than the difference of temperature.

A singular phenomenon connected with the radiation of caloric is the apparent radiation of cold. When a cold body, as a mass of ice, is placed in the focus of one of the mirrors, the thermometer in the opposite focus instantly suffers a reduction of temperature, greater as the cold of the body is more intense. The experiment was made at an early period by the Florentine Academicians, but it had not attracted notice until again performed by Pictet. Mr Leslie has since ascertained, that the phenomena, with regard to this apparent radiation of cold, are the same as in the radiation of heat, and the same laws are observed. It is greatest at a given temperature from a blackened surface, rather less from a surface of glass, and much less from one of metal; it is reflected by a metallic surface, but much less perfectly by a glass surface; and, in consequence of this, the frigorific effect is greatest when the bulb of the thermometer is of glass, and especially when it is blackened, while it is inconsiderable when the bulb is gilt. Hence the comparative powers of different surfaces in radiating, reflecting, and absorbing cold, are exactly the same as their powers of radiating, reflecting, and absorbing heat. The effects of interposed skreens too, Mr Leslie found to be similar. A metallic skreen completely arrests the frigorific effect, while one of glass al-

lows it to take place to a certain extent, more or less according to its proximity to the cold body.

Cold being merely the negation of heat, these results appear at first view extremely singular, and it becomes necessary to explain them in conformity to this principle. The diminution of temperature has been accordingly ascribed to the radiation of caloric from the thermometer; and in a general point of view this appears to be just, though there is some difficulty in explaining how the cold body acts in producing this radiation. Prevost supposed that there is a constant interchange of heat between bodies by radiation, the quantity radiated by each being less as the temperature is low; hence the thermometer in the focus of the mirror receives less caloric from the cold body in the opposite focus than it gives out, and its temperature falls,—an explanation liable to the difficulty of accounting for the effect of different surfaces in radiating cold; for according to the theory, the surface which radiates least caloric at a given temperature, that is, the metallic surface, ought to produce the greatest cold, while the fact is precisely the reverse. Pictet imagined, that while an equality of temperature exists among a number of contiguous bodies, the caloric is quiescent, or rather is in an equality of tension among them all, and there is no radiation from any of them, but when one is at a low temperature, caloric radiates towards it to restore the equilibrium. Hence the placing the cold body in the focus of the mirror, *causes* radiation from the bulb of the thermometer in the opposite focus, the mirrors serving to reflect it, and concentrate the effect. Mr Leslie has very happily applied his theory

of aërial pulsations to the same phenomenon,—the cold surface being supposed to abstract caloric from the contiguous layer of air, whence a momentary contraction follows, and a chain of pulsations, accompanied with discharges of heat, is established to the cold body by the medium of the mirrors from the thermometer. This hypothesis will of course be adopted only if the general theory of radiant heat depending on aërial pulsations be received.

SECT. IV.—*On the Comparative Quantities of Caloric contained in Bodies.*

CALORIC has a tendency to diffuse itself over matter until it produce an equilibrium of temperature. Hence, when a number of bodies unequally heated are placed near each other, a communication of caloric takes place, until a common temperature is established.

From this tendency to form an equality of temperature, it might perhaps be inferred, that caloric diffuses itself equally over matter; that it will therefore be contained in bodies in quantity proportional to the quantity of matter, or that equal weights of different portions of matter will contain at the same temperature equal quantities of this power.

This law is observed in the distribution of caloric in homogeneous bodies, different portions of the same kind of matter containing it proportional to their temperatures

and quantities of matter; or, at least the deviation, with regard to temperature, is inconsiderable, if it even exist.

But in heterogeneous bodies a different law is observed; each contains a quantity peculiar to itself, requisite to produce its temperature; nor are there perhaps any two bodies, which, in equal weights and at equal temperatures, contain the same quantity of caloric. This was first observed by Boerhaave, with regard to quicksilver and water. The subject was prosecuted by Black, Wilcke, Irvine, and Crawford; and from their researches the general law has been established, that at any temperature, different bodies, in equal quantities, whether estimated by weight or volume, contain unequal quantities of caloric.

This truth is established, when we attend to the augmentation of temperature in different bodies exposed to a common source of heat. They are, after a certain time, raised to a common temperature; but in suffering this rise, it will be found that they have absorbed very different quantities of caloric. Supposing, therefore, that at the commencement of the experiment they contained the same quantity, they must, at the temperature to which they are elevated, contain unequal quantities. But it might equally be proved, that their quantities must have been unequal at the temperature from which they were raised; for in beginning the experiment lower in the scale of heat, they would have required unequal quantities to raise them to this; and this arising from some property in the bodies themselves, which will always continue to operate, we may conclude, that at any temperature the quantities they contain are unequal. The same conclusion is established by

communicating an equal quantity of caloric to equal quantities of two bodies at the same temperature,—water and quicksilver for example; the augmentation of temperature which this will produce will be very different in each; it will amount to 28 degrees in the quicksilver, when it is only one in the water: we infer, therefore, that water requires 28 times more caloric than quicksilver to raise its temperature, and, of course, that at a given temperature it contains a quantity so much larger.

The general form of experiment by which this truth is demonstrated, and by which also the comparative quantities of caloric that bodies contain are determined, consists in mixing together determinate quantities of bodies at different temperatures, and observing the result; for the hotter communicating a portion of its caloric to the colder, we can, from the temperature that is established in the mixture, discover how much the temperature of the one has been diminished by the abstraction of this caloric, and how much that of the other has been raised by its communication, and, of course, we discover what quantity each requires to produce a given change.

In homogeneous bodies, the temperature produced by the mixture of equal portions of them at different temperatures is always the arithmetical mean between the temperature of each; the excess of caloric which the one contains above the other being equally divided between them, and producing the same rise of temperature in the one portion, as it does of reduction of temperature in the other. But when the same experiment is made with two heterogeneous bodies, the result is different; the tempera-

ture produced never being the mean of the two original temperatures. Thus, if one pound of water, at the temperature of 156, be mixed with one pound of mercury at the temperature of 40, the temperature which results is not the arithmetical mean, 98, but is not less than 152. This proves, that the change of temperature produced in the one by a certain quantity of caloric, is entirely different from that produced in the other by the same quantity; for the water in this experiment having had its temperature reduced from 156 to 152, has suffered a reduction of only 4 degrees; but the caloric which produced these have raised the temperature of the mercury not less than 112 degrees. The quantity of caloric, therefore, necessary to raise the temperature of one pound of water 4 degrees, is sufficient to raise that of an equal weight of mercury 112 degrees; or the quantity requisite to raise the temperature of one of these fluids one degree, raises the other 28. This will be the case at every temperature; and therefore at any point in the scale of heat, the quantity of caloric contained in water is to that contained in the same weight of mercury as 28 to 1.

If the experiment is varied by mixing water at a low, and mercury at a high temperature, the result is the same. If one pound of mercury, at 156, be mixed with one pound of water at 40, the temperature produced is 44. The mercury has been deprived of a quantity of caloric, which has reduced its temperature 112 degrees, and this quantity has raised that of the water 4. In this manner, when equal weights of two different bodies are mixed together, the temperature produced is always nearer to the

temperature of that body which contains the greatest quantity of caloric, because it requires the greatest quantity to produce in its temperature any change. The proportion is also indicated by the experiment; the comparative quantities of caloric contained in the two bodies being in the inverse ratio to the change of temperature in each by their mixture. The general formula, therefore, is to multiply the weight of each body by the number of degrees between its original temperature, and the common temperature obtained by their mixture. The comparative quantities of caloric they contain are inversely as the products.

When, instead of comparing the quantities of caloric which equal *weights* of different bodies contain, we compare the quantities contained in equal *volumes*, we still find that a similar difference exists. Thus the quantity of caloric necessary to raise the temperature of a given volume of water any number of degrees, is to that necessary to raise an equal volume of mercury the same number of degrees, as 2 to 1. This is therefore the proportion between the comparative quantities of caloric which these two bodies contain, estimated by their volumes; and similar differences exist with respect to every other kind of matter. The comparative quantities of caloric in bodies are usually estimated from equal weights of them; the experiments for this purpose being more easily executed with accuracy, than those by which they are estimated from equal volumes.

In making these experiments on solid bodies, the solid, heated to a certain temperature, generally to 212°, by immersion in boiling water, is transferred into a measured

portion of cold water, and the change of temperature in each is observed. In experiments in which water would enter into chemical combination with the body submitted to trial, some other substance must be used.

The mode of ascertaining the comparative quantities of caloric in bodies by mixture, is difficult of execution so as to attain perfect accuracy, from the sources of error to which it is exposed. A certain time is required before the common temperature is established, during which, part of the heat is abstracted by the vessel, and by the external air; and this is different in different cases, being influenced by the difference of specific gravity in the substances operated on, the facility with which they mix, their conducting powers, the quantities operated on, and the agitation communicated. Hence other methods have been proposed.

The principal of these is by an instrument contrived by Lavoisier and La Place. Ice, in melting, absorbs a quantity of caloric, which does not raise its temperature; this quantity being uniformly the same, or equal to what would raise the temperature of the same weight of ice-cold water 135 degrees of Fahrenheit's scale. If, therefore, any body at a high temperature be inclosed in a sphere of ice, so that the caloric it gives out in cooling is communicated entirely to the ice, the quantity which has been given out may be inferred from the quantity of ice melted, or water produced. On this is founded the construction of the Calorimeter, represented Plate II. Fig. 10. It consists of three vessels, A, B, C, adapted to each other, and inserted the one within the other, so as to leave

a cavity between the sides of each. A is a cage of iron net-work, and is designed to contain the body which is to be subjected to experiment, which, if solid, is placed within it, heated to a certain temperature; if liquid, is inclosed in a glass matrass. The second vessel, B, is designed to contain the ice, from the melting of which the quantity of caloric given out by the body in the first vessel is to be estimated. The ice, broken into small pieces, is supported on an iron grating at the bottom, through which the water filtrates, and is conveyed off by a pipe with a stopcock *a*, which comes from the bottom of the vessel. It has a double cover *b*, also adapted to it, capable of containing ice; the under part of this being perforated, so that the water which may be formed from the melting of any of the ice it contains may drop into the cavity itself, and can thus be collected to be measured. The third, or outer vessel, C, is similar in its construction to the second, and, like it, is to be filled with pounded ice, when the experiment is to be performed. The design of it is to prevent the agency of the external atmosphere, which, if above the temperature of 32°, would communicate caloric to the ice, and of course would contribute to its fusion, and prevent us from considering the quantity of water produced as a measure of the quantity of caloric which the hot body had given out; or if below 32°, it would abstract caloric, and lessen the quantity that would otherwise be melted. This is obviated, by placing pounded ice in the outer vessel, with a portion of water, the middle vessel being thus surrounded with a medium at the temperature of 32°. It has a double cover D, containing pounded ice,

and a tube and stop-cock, by which the water, when it accumulates, can be withdrawn.

This method is free from those sources of error to which the mode by mixture is liable. But it is exposed to others, which render its accuracy doubtful. It is difficult to estimate the quantity of water produced from the fusion of the ice; for a portion of it is retained by capillary attraction in the interstices of the mass; and from some observations, it appears, that a portion of the water produced in the upper part of the apparatus, in filtrating through the ice beneath, is again congealed, probably from the influence of the force of cohesion exerted from the surfaces of the fragments of ice.

The comparative quantities of caloric in bodies have been attempted to be estimated from observing the times equal volumes of them require to cool through a certain interval of the thermometric scale, the times being as their quantities estimated by the volume, and, if divided by the specific gravity of the substance operated on, as estimated by the weight. But the principle of this method appears not quite correct, the times of cooling being influenced by other circumstances, and particularly by the conducting and radiating power.

Some methods, too, have been proposed peculiar to the aërial fluids. The difficulties in ascertaining the quantities of caloric, corresponding with the changes of temperature in these by mixture, are extremely great, from the smallness of the quantity we can operate on, compared with the volume the air occupies. In the mode by the calorimeter, the errors from this source are some-

what diminished, from the quantity operated on being larger; the aërial fluid being passed through the instrument by a spiral tube, the temperature as it enters and passes out being ascertained by thermometers. But still the results are probably considerably remote from accuracy. Mr Leslie observed, that when a portion of air is rarified in a vessel, and time is allowed for its recovering the temperature of the surrounding medium, on admitting suddenly another portion of air into the partial vacuum, the rarified air is compressed; it hence gives out a quantity of caloric, and this, communicated to the air which has been admitted, raises its temperature. But the rise will be less, as this air requires more caloric to produce in it a given change of temperature; and therefore in operating on different aërial fluids, the comparative quantities may be discovered from the respective elevations of temperature. The method is extremely ingenious, but attended with considerable difficulties in the execution, so as to attain accurate results.

The property by which different bodies contain their respective quantities of caloric, has been termed the Capacity for Heat, or, adapting the expression to the modern nomenclature, the Capacity of a body for Caloric. This term is not designed to imply any theory with regard to the cause of this property, or the nature of it; nor does it present, as has been alleged, a vague or obscure idea. It is simply a general expression, to denote the property, in consequence of which, bodies contain at any given temperature, in equal quantities, peculiar quantities of caloric. That they do so is unquestionable, and it is convenient to

have a general term by which this can be expressed. The quantity contained in a body, and peculiar to it, has been named their Comparative, or their Specific heat. The phrase Specific Caloric is generally adopted.

What the nature of this property is, or from what cause different bodies require different quantities of caloric, to produce in them temperature to the same extent, is not easily determined. It is in general true, that bodies which are rare, have capacities for caloric greater than those which are more dense. It is even found, that we augment the capacity by diminishing the density of any body; the rarefaction of an aërial fluid, for example, in which this can be done to the greatest extent, being attended with a reduction of temperature from enlargement of capacity, and its condensation being followed by the opposite result. In liquids or in solids, condensation is likewise accompanied with a similar change from the same cause. But, although there is this general connection between the rarity of a body, and its capacity for caloric, it is not invariable or proportional; if it were, indeed, the quantities of caloric contained in bodies at given temperatures would be as their volumes,—a law which is far from being observed.

There must, therefore, be some other cause by which this is modified. If we regard caloric as a material substance subject to attraction, the attraction exerted to it by the substance in which it is contained might be supposed to be the cause modifying the law, which would otherwise be observed in its distribution, and by which, in consequence of its perfect elasticity, it would be contained in

bodies, in quantities proportional to the void spaces between their particles. But the relations of this agent are so imperfectly known, that no theory in which we can place much confidence can be given, and the fact must merely be stated as an ultimate one, that bodies require specific quantities of caloric for the production of temperature.

A question of some interest is, whether the peculiar relation of each body to caloric is the same at all temperatures; in other words, are their capacities for it uniform and permanent. It is possible this may not be the case; but that the rise of temperature itself, and the effects by which it is accompanied, may give rise to a change in the relation, so that a greater or less quantity of caloric may be required to produce a given rise of temperature, at a high than at a low part of the scale of heat. When the mechanical condition of a body is changed, when it passes to the fluid or aëriform state, this change of capacity actually happens. Does a similar change, though less perceptible at any particular stage, happen from the progressive expansion to which elevation of temperature gives rise?

The experiment by which this has been attempted to be determined, consists in mixing equal portions of the same body at different temperatures: if the capacity is permanent, the resulting temperature ought to be the arithmetical mean; for the hotter portion communicating the half of its excess of caloric to the colder, the one, if the capacity is the same in each, ought to suffer just as great a reduction as the other sustains an elevation

of temperature? But if the one portion had a greater capacity than the other, then the change it suffers must be less considerable, and the resulting temperature must approach nearer to its temperature than to that of the other, and of course deviate from the mean. The experiment is difficult of execution, so as to attain perfect accuracy, especially as no great range of temperature can be submitted to experiment, and as the difference in capacity, therefore, if it exist, cannot be expected to be great. Dr Crawford from his experiments was disposed to conclude, that the capacities of bodies are permanent; but he perhaps was somewhat influenced in drawing this conclusion by theoretical views. It appears to be more probable from theory, that the capacity should be progressive with regard to temperature, or should be greater in the higher than in the lower portions of the scale of heat; for this property is unquestionably to a certain extent connected with the density of bodies, being under a general point of view greater as they are less dense, and being increased in any body when its volume is enlarged; and, as rise of temperature is accompanied with enlargement of volume, this may be expected to give rise to augmentation of capacity. In any interval of temperature which we can measure this may not be considerable; but considered in relation to the whole scale, we cannot conjecture its amount, for we know not the extent of expansion from the commencement of the scale.

There is even reason to doubt if the permanence of capacity be established within the range of temperature at which bodies can be easily submitted to experiment. The

conclusion of Crawford rested very much on the previous assumption of the accuracy of the thermometer, and is invalidated if the expansions of the thermometrical liquid are progressive with regard to temperature, as this would counterbalance the effect from enlargement of capacity, if this happened, and give rise to an adjustment whence the effect of neither might be apparent. And, with regard to some bodies, it is ascertained, even by Crawford's own experiments, as well as by those of Gadolin, that the capacities are not permanent, but increase with the temperature, rendering therefore more probable the conclusion that this is a general result.

The law with regard to the distribution of caloric in bodies is of the first importance, as giving the theory of changes of temperature from chemical action. Combination is almost invariably attended with a change of capacity, the capacity of the compound not being the mean of the capacities of the bodies combined. When it is greater the temperature falls; when it is less the temperature is raised. On this principle are explained the production of heat in combustion, in respiration, and in a number of chemical combinations, and the production of cold in the solutions of salts in water, and in what are denominated freezing mixtures.

From the nature of the methods by which the quantities of caloric which bodies contain are ascertained, it is evident that we discover the comparative, not the absolute quantities. We find only how much caloric a body gives out, or absorbs, during a certain change of temperature; and by observing the change of temperature which the

body from which it has received, or to which it has given caloric, suffers, we may ascertain the comparative quantities necessary to produce equal changes of temperature in these bodies. But we do not learn the proportion which the quantity in each bears to the whole caloric which it contains; and therefore the capacities of different bodies are to be considered as merely comparative. Hence it becomes necessary to fix on one body as a standard to which the others may be referred. Water has been chosen as this standard; its capacity is stated at the arbitrary term of 1000, and with this the capacities of other bodies are compared. Thus the capacity of arterial blood is stated at 1030, indicating, that if at any temperature a certain quantity of water contain 1000 degrees of caloric, the same quantity of arterial blood at the same temperature will contain 1030 degrees. The capacities are usually referred to equal weights, not to equal volumes of bodies; but the latter are easily found, by multiplying the number expressing the specific caloric of any body estimated by its weight, by the number which denotes the specific gravity of the body; the product is the specific caloric estimated by the volume.

In the following table, the capacities of a number of bodies are stated as ascertained by Crawford, Irvine, Wilcke, Gadolin, Kirwan, Lavoisier, La Place and Dalton,—the initial letter annexed to each denoting the authority. I have inserted those only which have been ascertained by the method of mixture or by the calorimeter, those determined by other methods being more doubtful. I have also omitted several ascertained by the method

of mixture which still appear doubtful or unimportant. Where any difference in the capacity of the same substance, as ascertained by different experimenters, exists, this is pointed out by a reference to the different numbers. The table is subdivided, according as bodies exist in the aërial, the liquid, or the solid form, their capacities being different in these different states.

TABLE OF CAPACITIES.

Gases.

1	Hydrogen gas, - -	21.4000 C.
2	Oxygen gas, - - -	4.7490 —
3	Atmospheric air, - -	1.7900 —
4	Aqueous vapour, - -	1.5500 —
5	Carbonic acid gas, - -	1.0454 —
6	Nitrogen gas, - -	.7936 —

Liquids.

7	Alkohol, (12, 34) - -	1.0860 K.
8	Arterial blood, - -	1.0300 C.
9	Water, - - -	1.0000
10	Milk, - - -	.9999 C.
11	Solution of mur. of soda, 1 in 10 of water,	.9360 G.
12	Alkohol, (7, 34) - - -	.9300 Ir.
13	Sulphuric acid, diluted with 10 of water,	.9250 G.
14	Solution of muriate of soda in 6.4 of water,	.9050 —
15	Venous blood, - - -	.8928 C.
16	Sulphuric acid, with 5 parts of water, -	.8760 G.
17	Solution of muriate of soda in 5 of water,	.8680 —
18	Nitric acid, (30) - - -	.8440 K.
19	Solution of muriate of soda in 3.33 of water,	.8208 G.
20	——— nitrate of potash in 8 of water,	.8167 L.
21	——— muriate of soda in 2.8 of water,	.8020 G.
22	——— muriate of soda saturated, or in 2.69 of water, - -	.7930 G.

23	Colourless sulphuric acid, (41, 43, 44, 45)	.7580 —
24	Sulphuric acid, with 2 parts of water, -	.7490 G.
25	Solution of sulphate of soda in 2.9 of water,	.7280 —
26	Olive oil, - - -	.7100 —
27	Water of ammonia, specific gravity, 0.997,	.7080 —
28	Muriatic acid, specific gravity 1.122, -	.6800 —
29	Sulphuric acid, 4 parts with 5 of water,	.6631 L.
30	Nitric acid, specific gravity 1.29895, (18)	.6613 —
31	Mixture of nitric acid with lime, 9½ to 1,	.6189 —
32	Sulphuric acid, with an equal weight of water,	.6050 G.
33	4 parts with 3 of water, -	.6031 L.
34	Alkohol, (7, 12) - - -	.6021 C.
35	Nitrous acid, specific gravity 1.354, -	.5760 K.
36	Linseed oil, - - -	.5280 —
37	Spermaceti oil, - - -	.5000 C.
38	Sulphuric acid, with ½ of water, - -	.5000 G.
39	Oil of turpentine, (42) - -	.4720 K.
40	Sulphuric acid, with ¼ of water, -	.4420 G.
41	Sulphuric acid, (23, 43, 44, 45) - -	.4290 C.
42	Oil of turpentine, (39) - - -	.4000 Ir.
43	Sulphuric acid, concentrated and colourless, (23)	.3390 G.
44	——— specific gravity 1.87058, -	.3345 L.
45	(23, 41) - -	.3330 Ir.
46	Spermaceti melted, - - -	.3200 —
47	Quicksilver, specific gravity 13.30, -	.0330 K.
48	——— - - -	.0290 L.
49	——— - - -	.0290 W.
50	——— - - -	.0280 Ir.

Solids.

51	Ice, - - -	.9000 K.
52	—— - - -	.8000 Ir.
53	Beef of an ox, - - -	.7400 —
54	Rice, - - -	.5060 C.
55	Pease, - - -	.4920 —
56	Wheat, - - -	.4770 —
57	White wax, - - -	.4500 G.

58	Quicklime, with water, 16 to 9, -	.4391 L.
59	Barley, - - -	.4210 C.
60	Oats, - - -	.4160 —
61	Charcoal of birch-wood, (67) -	.3950 G.
62	Quicklime, (72, 74) - -	.3000 D.
63	——— saturated with water, and dried,	.2800 G.
64	Pit-coal, - - -	.2800 D.
65	——— - - -	.2777 C.
66	Chalk, (68, 75) - - -	.2700 D.
67	Charcoal, (61) - - -	.2631 C.
68	Chalk, (66, 75) - -	.2564 —
69	Sea-salt, (73) - - -	.2300 D.
70	White oxide of antimony washed, -	.2272 C.
71	Oxide of copper, - - -	.2272 —
72	Quicklime, (62, 74) - -	.2239 —
73	Muriate of soda in crystals, (69) -	.2260 G.
74	Quicklime, (62, 72) - -	.2168 L.
75	Chalk, (66, 68) - - -	.2070 G.
76	Crown glass, - - -	.2000 Ir.
77	Agate, specific gravity 2648, -	.1950 W.
78	Flint-glass, specific gravity 287, (81) -	.1900 D.
79	Sulphur, - - -	.1900 —
80	——— (84) - - -	.1890 Ir.
81	White glass, specific gravity 2.886, (78)	.1870 W.
82	White clay burnt, - -	.1850 G.
83	Black lead, - - -	.1830 —
84	Sulphur, (79, 80) - -	.1830 K.
85	Oxide of antimony, - -	.1666 C.
86	Iron, (89, 91, 92, 95) - -	.1450 Ir.
87	Oxide of zinc, - - -	.1369 C.
88	White cast iron, - - -	.1320 G.
89	Iron, - - -	.1300 D.
90	White oxide of arsenic, - -	.1260 G.
91	Iron, (86, 89, 92, 95) - -	.1269 C.
92	Iron, specific gravity 7876, - -	.1260 W.
93	Hardened steel, - - -	.1230 —
94	Steel softened by fire, - -	.1200 —

95	Soft bar iron, specific gravity 7.724, (86, 89)	.1190 G.
96	Brass, specific gravity 8356, (98) -	.1160 W.
97	Copper, specific gravity 8.785, (99) -	.1140 W.
98	Brass, (96) - - -	.1123 C.
99	Copper, (97) - - -	.1111 —
100	Sheet Iron, - - -	.1099 L.
101	Zinc, specific gravity 7154, (107) -	.1020 W.
102	—— - - -	.1000 D.
103	Nickel, - - -	.1000 —
104	White oxide of tin, - -	.0990 C.
105	Hammered copper, specific gravity 9150,	.0970 G.
106	Oxide of tin, (104) - -	.0960 K.
107	Zinc, (101) - - -	.0943 C.
108	Sublimed arsenic, - -	.0840 G.
109	Silver, specific gravity 10.001, -	.0820 W.
110	Tin, (115) - - -	.0704 G.
111	Yellow oxide of lead, - -	.0680 —
112	White lead, - - -	.0670 —
113	Antimony, - - -	.0645 —
114	———— specific gravity 6107, -	.0630 W.
115	Tin, specific gravity 7380, (110) -	.0600 W.
116	Red oxide of lead, - - -	.0590 G.
117	Gold, specific gravity 1904, -	.0500 W.
118	Vitrified oxide of lead, - -	.0490 G.
119	Bismuth, specific gravity 9861, -	.0430 W.
120	Lead, specific gravity 1145, -	.0420 W.
121	—— - - -	.0352 C.

Sect. V.—*Of the Quantities of Caloric which Different Forms of the same Body contain.*

Besides the general law which has been demonstrated, that different bodies, in equal weights and at equal temperatures, contain unequal quantities of caloric, it has further been established, that a similar law exists with respect to the same body in its different states of aggregation: a body in the fluid form contains more caloric, or requires a larger quantity to produce a given change of temperature in it, than it does while solid; and in the state of air or vapour, it requires still more caloric than it does in the liquid form. Hence, when a solid is melted, or a liquid is converted into vapour, a quantity of caloric is absorbed, which has no effect in producing augmentation of temperature. This gives rise to the phenomena of what has been denominated Latent Heat, for the discovery of which we are indebted to Black.

The truth of the fact is sufficiently evident, when the phenomena attending liquefaction and vaporization are attentively examined. When caloric is communicated to a solid body, increase of temperature is produced, and this continues to proceed while the caloric continues to be added, until the body arrives at its melting point: but whenever it begins to melt, the rise of temperature ceases, though the addition of caloric be continued as before; and the fluid, as it forms, remains at one point until the fusion is completed. In this case, then, it is evident, that

a quantity of caloric disappears; for it continues to be added to the body, but has no effect in raising its temperature. The case is the same when a liquid is converted into vapour. Its temperature is first raised to the point at which it begins to boil, by the communication of caloric; but though the communication be still continued, the temperature, neither of the fluid which is evaporating, nor of the vapour rising from it, is farther raised, but remains stationary at that degree in the thermometrical scale at which the conversion into vapour commenced, until the whole be evaporated. It is evident, therefore, that in this case also a quantity of caloric is absorbed by the vapour formed, which has no effect in raising its temperature. The liquid or vapour, after it is formed, has its temperature raised by additions of caloric.

It was from considering these facts, that Dr Black concluded, that during liquefaction and vaporization a quantity of caloric is lost, becomes latent, or passes into the body without raising its temperature,—a conclusion which he established by very simple but decisive experiments, affording an admirable example of chemical research.

To prove it with regard to liquefaction, he placed equal portions of water in two vessels, cooling the one portion to 32°, and causing the other to freeze, but taking care that the ice should not be lower than this temperature. They were equally exposed to an atmosphere somewhat warmer, from which of course they received heat,—the temperature of the water soon rose, and, at the end of half an hour, the rise amounted to 7°. But the temperature of the ice remained stationary at 32, though it must have received caloric equally with the other. It merely began to

melt; it continued to do so slowly, and for its entire fusion 10½ hours were required, during which its temperature continued the same. Now, judging from the rise of temperature which the water had sustained in half an hour, and assuming, what there can be no doubt of, that the ice received caloric equally with the water, in the time required to melt it, it must have absorbed a quantity of caloric equal to what would have raised the temperature of the same weight of water 139°, yet it suffered no augmentation of temperature. This result was confirmed by an experiment made in a different manner, in which the disappearance of a large portion of caloric is rendered still more striking,—adding a given weight of ice at 32° to the same weight of water at the temperature of 172. The ice was melted, but the temperature of the whole liquid was only 32; a quantity of caloric, therefore, which raised the temperature of water 140°, had in this, as in the former experiment, disappeared.

The caloric thus absorbed by ice in melting, Dr Black found is again given out when water is congealed. This, he observed, is evident from the temperature of freezing water being stationary at 32°, though the temperature of the surrounding medium may be much lower than this; the water, as it passes to the solid state, giving out the caloric it had absorbed when it was formed: whatever may be the celerity of the freezing from the cold of the surrounding medium, the evolution of caloric must always be proportional to it, and hence the temperature cannot be reduced until the whole is congealed. The temperature of the ice will then fall to that of the matter around it.

This evolution of heat in congelation, Dr Black rendered more sensible by direct experiment. Having added a little salt to a portion of water, so as to enable it to sustain reduction of temperature below 32° without freezing, he exposed it, with a similar portion of water in another vessel, to a cold atmosphere. Both were cooled with regularity to 32°; but at this temperature the pure water remained stationary, while that with the salt dissolved in it continued to fall lower; the former must equally have suffered an abstraction of caloric with the latter, but caloric being evolved from its congelation prevented its fall. In another experiment, Dr Black cooled water, by avoiding agitation, a number of degrees below its usual freezing point, 32°: on agitating it, it congealed, and the temperature instantly rose to 32° from the evolution of the caloric peculiar to it in the state of water.

Similar experiments were made by Irvine on spermaceti, wax, and tin; they have since been extended to other bodies, and with regard to all the same law has been established, a portion of caloric peculiar to each being absorbed when the body melts, without causing any rise of temperature, and this portion of caloric concealed in the liquid becoming sensible again when it is congealed.

Dr Black demonstrated, that a similar phenomenon accompanies the other change of state to which bodies are subject, that into vapour or air, a quantity of caloric being absorbed by the body passing into this state without raising its temperature, and being evolved when it returns to the liquid form. This, as has been remarked, is even evident from the usual phenomena of vaporization atten-

tively examined, neither the liquid nor the vapour rising from it suffering any increase of temperature after the ebullition has commenced, though caloric be constantly communicated. It was farther established by experiments ascertaining it with more accuracy, or placing it in a clearer light.

A portion of water in a cylindrical tin vessel placed on a heated iron plate, was raised in temperature from 50 to 212° in four minutes, when it began to boil; in that time, therefore, it had received a quantity of caloric capable of raising its temperature 162°. It continued to boil, and twenty minutes elapsed before it was dissipated; neither its temperature, nor that of the vapour into which it was converted, rose above 212°, yet it must have continued to receive caloric as before; that is, at the rate of 162° every four minutes; of course, in its vaporization, a quantity of caloric had been absorbed, which, applied at once, would have been equal to raising its temperature 810°.

A liquid heated under pressure may have its temperature raised above its usual boiling point, the transition into vapour being prevented. A quantity of water included in a strong phial closely corked, with a thermometer included, was heated to 222°: the cork was suddenly withdrawn, a small quantity only of vapour rushed out, and the remaining water instantly fell to 212°. This experiment Mr Watt repeated on a much larger scale, water being heated in a copper digester with a safety valve to a much higher temperature; yet, on opening the valve, instead of the whole escaping in vapour, not more than one-third of it assumed this state, and the temperature

of the remaining portion sunk as in the preceding experiment.

A similar absorption of caloric attends the vaporization of volatile liquids at a common temperature, producing therefore sensible cold, greater as the liquid is more volatile, or as the change is accelerated, as Cullen observed.

The caloric which is thus absorbed in the transition of a body to the state of vapour, is again evolved when the vapour is condensed. Dr Black found, that when steam, at the temperature of 212°, is condensed by being received in cold water, the temperature of this is much more raised, than by the communication of a weight of water at 212° equal to that of the steam. And Mr Watt having condensed steam in a metallic tube, by suddenly forcing down a piston accurately adapted to it, the end of the tube being placed in water, found a quantity of caloric communicated to the water, equal to what would have raised the temperature of a portion of it equal in weight to the steam 943 degrees. Yet the tube and the included steam, previous to the condensation, were at the temperature only of 212°.

All these facts prove the truth of the general proposition, that when bodies pass from the solid to the fluid, or from the fluid to the gaseous state, a quantity of caloric is absorbed, which has no effect in raising the temperature of the body in its new form, this caloric being again evolved when the body returns to its former state. This portion of caloric absorbed during these changes. and not discoverable by the usual effect of raising temperature, Black named Latent Heat, in opposition to the portion by which tem-

perature is produced, and which he denominated Sensible Heat.

In assigning the cause of these phenomena, Dr Black supposed, that the caloric which disappears or becomes latent, produces the change of form, losing at the same time its own characteristic properties, probably by entering into a species of combination with the matter on which it operates. "Fluidity," says he, "I consider as depending immediately and inseparably on a certain quantity of the matter of heat which is combined with the fluid body in a particular manner, so as not to be communicable to a thermometer or to other bodies, but capable of being extricated again by other methods, and of re-assuming the form of moveable or communicable heat." And, again, with regard to vaporization, "when a fluid body is raised to its boiling temperature by the continual and copious application of heat, its particles suddenly attract to themselves a great quantity of heat, and by this combination their mutual relation is so changed, that they no longer attract each other, but separating, compose a fluid elastic and expansive like air. This new form of aggregation, (taking the example of water,) is the effect of a new combination of heat with the primary particles of water, and is a sufficient indication of this union, in the same manner as fluidity was a sufficient mark of a sudden and copious combination of heat with the particles of ice."

A very different theory of these phenomena, and more approaching to a philosophical generalization, was advanced by Dr Irvine. Temperature depends not merely on the action of caloric, but on its action modified by that

peculiar relation of bodies to it which we denominate their capacity. If the capacity of a body be enlarged, the quantity of caloric communicated to it remaining the same, its temperature must fall; if the capacity be diminished under the same condition, its temperature must rise; or if the capacity be enlarged while caloric is proportionally communicated, this caloric will be absorbed by the body, and remain in it without any increase of temperature. Now this, Dr Irvine conceived, is what happens in fluidity and vaporization. The sensible caloric communicated, and raising the temperature of the body to its melting, or to its vaporific point, weakens progressively its cohesion, and at length so far changes its state of aggregation, as to admit of a new arrangement of its parts, constituting first fluidity, and afterwards the state of vapour or air. These changes, Dr Irvine supposed to be accompanied with a change of capacity, the capacity of the body in its liquid being greater than in its solid state, and becoming still larger in the state of vapour. If this be admitted, it necessarily follows, that a quantity of caloric must be absorbed by the body in passing into the liquid and aërial forms, which shall have no effect in augmenting its temperature, and which, of course, is not discoverable in it by the thermometer. But there is no reason to believe that this caloric has lost its properties, has entered into any peculiar combination with the body, or is in any state different from the rest of the caloric it contains. It goes with that caloric to sustain the temperature, and it has been absorbed without raising temperature, merely because the capacity of the body has been enlarged; and when

the capacity is diminished, as happens in the reverse change of form, it is, of course, again evolved. A body in one form, in a word, contains more caloric than in another form at a given temperature, exactly as one body contains more than another does; or, according to this theory, the cause why water contains more caloric than ice at 32°, is the same as that by which water contains more caloric than quicksilver; and were it possible to convert quicksilver into water by a process similar to that by which we convert ice into water, we should have precisely the phenomena of latent heat.

The whole question, therefore, on this subject, is with regard to the assumption on which the theory rests, whether an augmentation of capacity accompanies liquefaction and vaporization or not. No doubt can remain of its superiority *à priori*, to the opinion of Black. It explains the phenomena; for it is obvious, that if by fusion or vaporization the capacity of a body be enlarged, either its temperature must fall, or caloric must be absorbed without producing any rise of temperature: the first cannot happen; for, in this case, the temperature of the body falling below its fusing or vaporific point, the change of form could not proceed: the second event, therefore, must be that which will occur, or if, by applying caloric, we raise and preserve the temperature sufficiently high to cause the transition of form to proceed, if this be accompanied with an increase of capacity, the caloric applied must be absorbed and become latent, or occasion no increase of temperature. And the theory has farther the very important advantage, that while the opposite system

is an insulated hypothesis, framed to account for this particular case, Irvine's is an extension by generalization of a law, proved to exist with regard at least to different bodies, and not unlikely to operate in a similar manner on the same body in different forms.

The determination of the fact occupied the attention of Dr Irvine for a series of years, the experiments by which only it could be decided being attended with peculiar difficulties; for, in determining the capacity of the body, either in the solid or liquid state, it is necessary, that in the progress of the experiment it should not change its form. Ice, therefore, must be operated on at temperatures below 32°, and water at temperatures above this. Dr Irvine employed the medium of a third substance, such as quicksilver, river-sand, or iron-filings, which he added to each, and determined the capacity in the usual manner; and he uniformly found, that the capacity of water is greater than that of ice, and in a ratio which he inferred, from the average of his experiments, to be as 10 to 8. A similar augmentation of capacity Dr Crawford found to take place when water is converted into vapour. It is proved then, that the change in the relation of the body to caloric is not confined, as Dr Black's hypothesis supposes, to the moment of liquefaction or vaporization, but that at these changes the relation is so altered, that henceforth the liquid requires more caloric than the solid did to raise it every degree of the thermometric scale, and the vapour, in like manner, requires more than the liquid. In consequence of this, an absorption of caloric must take place at the moment of change, sufficient with the caloric

the body contained, to keep up the existing temperature from the point of absolute privation, according to the enlarged capacity of the body in its new state. And with the admission of these facts, the one theory is demonstrated, while the other cannot be maintained.

The only difficulty that has been urged against the theory of Irvine, of any seeming importance, is that of accounting for the change of form; for since the temperature of the liquid is not sensibly greater than that of the solid from which it is formed, nor that of the vapour greater than that of the liquid from which it rises, it has been contended, that the change cannot be ascribed to the operation of sensible caloric, and must therefore be ascribed to the action of at least a portion of that which becomes latent. The difficulty, however, is in a great measure, perhaps, entirely obviated by considering the change of form as arising from the expansive operation of caloric, increasing as it is accumulated, until it sufficiently modify or subvert the force of cohesion to admit of fluidity and vaporization being established; and this being progressively exerted, the ultimate effect may take place at a point in the scale of temperature indivisible, so that we shall be unable to discover a difference of temperature on the one hand, or on the other.

This view of the cause of the change of form is confirmed, by finding the change produced by causes which must operate solely by altering the distances at which the particles of bodies are placed. Thus, the transition into vapour is effected by withdrawing pressure, which can be an antagonist only to the expansive operation of sensible

caloric: Or, by applying pressure, a vapour may be reduced to the liquid state, though this pressure can have only a mechanical effect, approximating the particles, and cannot subvert any chemical combination of caloric, did it exist.

It may therefore be concluded, that the absorption of caloric which accompanies liquefaction and vaporization, is owing not to any chemical combination, but to the enlarged capacity which the body acquires by a change of form. It may be supposed, indeed, that the difficulty in this view of the subject is only avoided, not removed. May not this very difference of capacity in bodies, in whatever state they exist, proceed from a chemical combination of caloric? By saying that different bodies, or different forms of the same body, have different capacities for caloric, the general fact is merely expressed, that in equal quantities, and at equal temperatures, they contain unequal quantities of this power. But the cause of this is not assigned. May it not then be chemical combination of part of the caloric, of that part of it in each body which amounts to the difference of the quantity it contains, compared with another? This opinion is at once refuted by the consideration, that, were it true, the quantity of free caloric, or caloric of temperature, ought in all bodies to be the same, and that consequently in equal changes of temperature, equal quantities of caloric ought to be absorbed, or given out by all, since the very principle which is assumed is, that the cause of the difference in the absolute quantities of caloric which bodies contain is, that that portion in one body, which exceeds what is con-

tained in another, exists in it in a state of chemical combination.

Whether, therefore, the question be considered as relating to the cause, why different bodies contain, at the same temperature, unequal quantities of caloric, or to the cause why different forms of the same body follow the same law, in neither case is it probable that a chemical combination of part of that caloric gives rise to the difference. *And as the phenomena are in both cases the same, they must be ascribed to the same cause.* Until this is discovered, the general fact ought merely to be expressed: Caloric, whether matter or motion, is to be considered as a power diffused over matter, as the cause of that state of bodies termed their temperature, as having a tendency to diffuse itself, until a common temperature is formed; but for the production of this temperature in different bodies, and in equal forms of the same body, unequal quantities of this power are required. If it be a material agent, the difference in the quantity contained may be owing to the specific attraction exerted by each body; but still this attraction is merely the force by which the whole quantity is retained, and does not operate more on one portion than on another.

Some philosophers of eminence, indeed, without alleging that the difference in the quantities of caloric in different bodies, or the absorption of it during liquefaction and vaporization, is owing to chemical combination, have supposed, that there may be a portion of caloric existing in bodies in such a state of combination. Lavoisier and La Place inclined to this opinion, from finding by experi-

ment, that in different cases of chemical union, or of change of form, the quantity of caloric rendered sensible does not correspond with the changes of capacity that take place, but is sometimes greater, at other times less; whence they concluded, that a portion of caloric must exist in bodies in some other state, and probably in more intimate combination. They admit, however, that trivial errors in the estimation of the capacities might have given rise to the apparently discordant results they obtained; and when the sources of fallacy attending such experiments are considered, it will appear not improbable that such errors must have been present. Irvine and Crawford devoted much attention to this investigation, and uniformly found, that when bodies produce heat by mutual action, or change of form, their capacities are diminished, and that, on the contrary, when they produced cold their capacities were increased; nor were the results inconsistent with the law of the changes of temperature being proportional to the increase or diminution of capacity, making allowance for the inaccuracies to which such experiments are unavoidably liable. Gadolin executed a very extensive series of experiments with the same view, and drew from them the same conclusion. Nor are there any facts which, when duly considered, can be regarded as affording proof, that any portion of caloric exists in bodies chemically combined. The hypothesis, however, has often been maintained, and the language implying it is often used by chemists, as if it were established. It is therefore necessary to remark, that it rests on no just grounds. The different quantities of caloric contained in bodies, re-

gulated by what we name their capacities, cannot be referred to the operation of any peculiar force different from that by which the whole quantity of caloric is contained; neither can the absorption and latent state of the caloric, absorbed in liquefaction and vaporization, be referred to this cause. And we have no reason to believe that any other portion of caloric exists in bodies in a combined state. The agency and relations of this power are indeed so peculiar, that, even admitting its materiality, we can place little reliance on any conclusion with regard to its mode of existence, not established by direct evidence, but resting on analogies transferred from ponderable substances.

From the enlargement of capacity and consequent absorption of caloric, which attends liquefaction and vaporization, some interesting applications both to natural phenomena and to purposes of utility are derived.

Such, for example, is the fixity and uniformity of the temperature at which bodies melt. Ice melts at 32° of Fahrenheit, and, when raised to this temperature, the farther communication of caloric, however rapid, has no effect in raising its temperature, till the whole is converted into water; since, as quickly as the ice is melted, as quickly is the caloric absorbed by the fluid. Were it not for this absorption of caloric, the liquefaction of ice and snow, in the colder climates, at the approach of spring, would take place almost instantaneously, when the temperature of the atmosphere rose above 32°; whereas, from this, the

melting is gradual and progressive; the water that is formed is distributed more slowly, and the too sudden rise of temperature, which in such climates would prove fatal to vegetables, is prevented. The reverse of this, too, or the extrication of caloric, when water is converted into ice, is equally beneficial; since, were it otherwise, the freezing of large collections of water would be extremely rapid when the temperature of the atmosphere fell below 32°. But, from this extrication, the freezing is gradual, and a large quantity of caloric is given out by the water in passing to the solid state, by which the approaching cold is moderated, and the congelation rendered more slow.

Similar general effects arise from the operation of this law in vaporization. When the earth is much heated by the sun's rays, water is evaporated from its surface, and from rivers and the ocean, and the conversion of this into vapour is necessarily accompanied with the absorption of caloric. Hence evaporation is the most powerful agent employed by nature to moderate excessive heat. On the contrary, when the vapour of the atmosphere is condensed by cold, and descends in rain or snow, it gives out the caloric it had received, which is then beneficial rather than hurtful.

The process of artificial refrigeration is explained on the same principle. By allowing water to filtrate slowly through porous earthen vessels, so as to present an extensive humid surface to the atmosphere, it passes rapidly into vapour, and in this vaporization absorbs so much caloric as to produce a considerable degree of cold. Liquors are cooled, and in warm climates ice formed, by arrange-

ments of this kind, even when the temperature of the atmosphere is above 32°.

The theory of freezing mixtures is likewise deduced from the doctrine of latent caloric. These are mixtures of saline substances, which, at the common temperature, by their mutual chemical action, pass rapidly into the fluid form, or are capable of being rapidly dissolved in water, and, by this transition to fluidity, absorb caloric, and produce degrees of cold more or less intense.

The use of steam as a vehicle and source of heat, affords an example of the scientific application of these principles. By conveying it into water, it is condensed, and by the evolution of the latent caloric by the condensation, the temperature of the water is raised, so as soon to arrive at 212°. Where large quantities of water are to be heated, this method has superior advantages, as by having a common boiler, from which the vapour is conveyed by tubes, the loss of heat is much less than if fire was applied to different vessels, and the vessels are subject to less wear, and may be constructed at less expence. Another application of the same principles is that of heating apartments by conveying steam through tubes, proposed in an early volume of the Philosophical Transactions, and since revived. The steam in its progress is condensed gradually, and gives out its latent caloric, so as to produce an equable warmth.

The modern improvements in the Steam-engine, as they originated from Dr Black's discovery, so they afford a very striking exemplification of the doctrine of latent caloric. In the engine wrought previous to the improve-

ments of Mr Watt, the steam was received into a cylinder, to which a piston was adapted, which was raised by the introduction of steam: this was condensed by a jet of cold water, and the piston was of course forced down by the pressure of the atmosphere, and by these alternate actions the machine was worked. But this was attended with an immense loss of heat; for by the jet of cold water not only was the steam condensed, but the cylinder was likewise cooled, as it was also by the entrance of the atmospheric air, and the first portion of steam, therefore, that entered was condensed. At each stroke of the engine this waste is repeated, and thus, according to Mr Watt's calculation, at least half of the steam produced in the boiler is lost. His principal improvements consisted in condensing the steam, not in the cylinder, but in another vessel communicating with it by a pipe with a valve, and in excluding from the cylinder the atmospheric air, and depressing the piston by steam introduced above it, and condensed in the condensing vessel alternately with the steam beneath. The whole can thus be kept at the temperature of 212°, and the immense waste of heat in the old method is obviated.

Sect. VI.—*Of the Absolute Quantity of Caloric in Bodies.*

A problem which the Chemists have sometimes proposed for solution, is that of determining the whole quantity of caloric in bodies, and of course at what distance, mea-

sured by thermometrical degrees from a given temperature, the point of absolute privation, or what they have named the real zero, would be placed. It is obvious, that any reduction of temperature that we can command is far distant from the total abstraction of caloric, and it is only by calculation from certain known facts that the zero can be determined.

The possibility of this occurred to Dr Irvine, and the principles on which his method were founded are extremely simple. Assuming that the caloric contained in bodies is as their capacities, and knowing the difference between the capacity of a body in its different states, for example in its solid and liquid states, it is obvious, that if we ascertain, by experiment, the quantity of caloric which it absorbs or gives out in passing from one state to the other, we can determine the whole quantity of caloric it contains; for the quantity evolved bears a certain proportion to this, which proportion the difference of capacity gives. Thus, if the capacity of water be 10, and that of ice 9, and if the whole quantity of caloric which each contains be as its capacity, then water contains a quantity as 10, ice a quantity as 9, or water contains one-tenth more caloric than ice at the same temperature. This tenth part, of course, is given out when water passes into the state of ice; the quantity actually evolved by it we discover by experiment to be equal to what would raise its temperature 140° of Fahrenheit's scale. The water previous to freezing, therefore, contained a quantity equal to ten times this, or a quantity equal to what would elevate its temperature 1400°. Of course, at this distance from 32° of Fahrenheit, it

would be wholly deprived of caloric, or the real zero would be placed; and this would be the same with regard to all bodies measured by thermometrical degrees, according to the capacity of each; for although they contain different quantities, this is only because they require different quantities to produce the same elevation of temperature: the degrees of temperature are the same.

The calculation of Irvine was confirmed by the experiments of Crawford, and also by those of Gadolin, both made on the capacities of bodies combining together, the capacity of the compound formed, and the quantity of caloric absorbed or evolved during the combination. Crawford, by determining the capacity of water, the capacities of its constituent principles, and the quantity of caloric evolved when these combine, found the zero to be at 1532 below the freezing point of water; and Gadolin, from observing the changes of temperature in the solution of muriate of soda in water, and also in the combination of sulphuric acid and water, compared with the capacities of the respective substances, placed it at 1432 below that point. Other chemists, however, have obtained results extremely discordant. In the experiments of Lavoisier and La Place, the numbers are very remote from those above stated, and from each other; and, in the more recent experiments of Dalton, are so even to a greater extent; the zero being found, from some experiments, at 3000, others at 5000, or at 7000° below the temperature of freezing water. We can, of course, place little confidence in any of these calculations; and either the assumption on which the theorem rests, that the quantity of calo-

ric in bodies is as their capacity, is incorrect; or the experiments, so far as relates to the estimation of the capacities, must be liable to sources of error nearly unavoidable, and which, from being multiplied by the calculation, give rise, even though trivial in themselves, to errors so great. The latter is probably the case; for the methods of discovering the capacities of bodies, give us rather approximations than absolutely accurate results.

From the diversity of opinions which has prevailed with regard to the state in which caloric exists in bodies, several forms of expression have been introduced, and are still in use, which it may be proper to define.

Free caloric is caloric in that state in which it expands bodies, and, accumulated to a certain extent, occasions the sensation of heat. It is synonymous with the *sensible heat* of Dr Black, and with the *caloric of temperature* of other chemists.

Specific caloric is the quantity of caloric peculiar to any body compared with another, and therefore expresses the relative quantities of caloric contained in equal weights of different bodies at the same temperature. It is synonymous with the *comparative heat* of Dr Crawford. Others have used the phrase *relative heat* in a similar sense. This, however, is employed by Wilcke to denote the specific caloric of a body, estimated, not by the weight, but by the volume.

The disposition or property by which different bodies contain certain quantities of caloric, at any temperature, is termed their *capacity* for *caloric*.

Latent caloric, or *latent heat*, is the expression used to denote that quantity of caloric which a body absorbs, when it changes its form. *Combined caloric* is that portion supposed to be contained in any body, in a state of chemical combination. The *Absolute Heat* of Crawford denotes the whole quantity of caloric which any body contains; and is expressed, according to the modern chemical language, by saying, the absolute quantities of caloric present in bodies.

Sect. VII.—*Of the Nature of Caloric.*

By the ancient philosophers, the cause of heat was considered as a peculiar subtle fluid or element; and this opinion was received until the time of Bacon. From observing that the circumstances which cause augmentation of temperature are such as excite motion, and that in general whatever produces motion produces heat, he advanced the hypothesis, that the heated state of bodies depends merely on vibration of their particles. Though this opinion was adopted by some chemists, particularly by Boyle, Newton, and Macquer, the other, which considers the phenomena of heated bodies as depending on the presence of a peculiar material principle, continued to be more generally received.

The general phenomena which are produced by the action of caloric, are sufficiently explained on the hypothesis of its being a subtle highly elastic fluid, capable of pene-

trating bodies, with the exception of one familiar phenomenon,—the excitation of heat by friction, percussion, or any species of motion producing vibration in the particles of bodies. On the hypothesis of temperature depending on the presence of a material agent, it is difficult to conceive how it should be raised by the operation of these causes, and it is from this difficulty that the hypothesis of its depending on motion has originated.

The difficulty has appeared greater, too, since the excitation of temperature by friction has been investigated with more precision; for it appears to be produced without limitation while the friction is applied, and without any external source whence it may be supplied. Rumford observed, that in the boring of cannon, much heat is rendered sensible by the friction. To ascertain its quantity with more accuracy, he placed a solid cylinder of brass in a trough with water, and applied the borer to it in the usual manner. In an hour the temperature had risen from 60 to 107, and in two hours and a half the water was brought to boil, its quantity being 18 libs., and the apparatus immersed in it, which was of course likewise heated to 212°, being equal to 15 libs. This excitation of heat, it was obvious, was independent on any action of air, as this was excluded by the manner of making the experiment: the water does not appear to have exerted any chemical agency, as it suffered no change: the caloric, Rumford supposed, could not be derived from the surrounding matter, as this was actually receiving heat from the body submitted to friction, and it could not, he conceives, be derived from this body itself from any diminution of capacity produced by

the friction, as the capacity of the borings of the metal he found to be the same with that of the mass of metal. He concludes, therefore, that what was thus furnished, apparently without limitation, could not be material, and that it is difficult to conceive of any thing capable of being excited in the manner the heat was excited and communicated in these experiments, except motion. Experiments giving a similar result were published nearly at the same time by Mr Davy.

In comparing the two hypotheses thus advanced on the nature of caloric, little doubt can remain of the superiority of that which regards it as a material principle; for the general phenomena connected with its operation receive a satisfactory explanation from this assumption, at least with the exception of the difficulty now stated; while, on the opposite hypothesis, that it arises from vibration or motion of the particles of matter, these phenomena are very imperfectly explained. Expansion, fluidity, and vaporization, may be conceived to arise from the introduction of an elastic fluid counteracting the mutual attraction of the particles of matter: this fluid, it is sufficiently probable *à priori*, may have peculiar relations to different bodies, may therefore be propagated through them with different degrees of facility, be contained in them in a given state in unequal quantities, or may act upon them unequally, so as in equal quantities to produce unequal effects. Considering caloric, on the other hand, as arising from vibration, it is not obvious how this should produce even the most general effect, that of expansion: we do not perceive how, when accumulated to a certain

extent, it should give rise to permanent repulsion: we are equally at a loss to account for the law which regulates its distribution in bodies, as producing temperature, or the laws of its communication, which are different from those of motion.

To establish this superiority more decidedly, there remains to be explained, on the assumption of the materiality of caloric, its excitation by friction. Is the following hypothesis adequate to this? By friction, or similar causes of motion, the particles of bodies are thrown into a state of vibration; they alternately approach to, and recede from each other. In their approach, the common law with regard to the effect of condensation on temperature must be observed, or heat will be excited; in the corresponding retrocession, heat will, no doubt, from the same cause, be absorbed. Now, is it possible, that in this retrocession the layer of matter, in the state of vibration, may rather receive caloric from the contiguous layer, and ultimately from the rest of the mass, than re-absorb that which had been evolved in the preceding approximation, that in this way a current of caloric may flow towards the vibrating surface, and a constant evolution of it be kept up? The possibility of this will perhaps be established by proving, that an analogous case occurs in which this happens. The excitation of electricity by friction affords it. The surface affording electricity is in a state of vibration from the friction applied to it; and the phenomena of electricity prove, that the electric fluid forced out, probably by the approximation of the particles from the vibration, is not re-absorbed in the following retrocession, but forms

an atmosphere around the electric body, or is carried off by the surrounding matter, while a new portion is received from the mass in contact with the excited surface, and ultimately from the earth, so that a constant evolution of it can be continued, while the friction is applied. Caloric may follow the same law, though, from not having that relation which electricity has with regard to conducting and non-conducting matter, this is not so easily established. If it do operate, it may give rise to similar phenomena, at least to a less extent.

The evolution of caloric, from this cause, is no doubt connected with diminution of capacity; and that this should happen, is even rendered extremely probable, from the effect of condensation on the capacities of bodies, as already illustrated. But this diminution of capacity is only momentary, though constantly renewed; and the experiment, therefore, by Rumford, of ascertaining the capacity after the friction has ceased, is wholly inconclusive. It is farther to be remarked, that a very slight diminution of volume may be sufficient to produce a considerable elevation of temperature. Berthollet has justly remarked, with regard to Rumford's experiment, that a very large addition of caloric is requisite to produce even a small augmentation of volume in a mass of solid metal, and that of course a small reduction of volume, and therefore an approximation of the particles, during friction, far from considerable, may evolve a large quantity of heat.

The conveyance of caloric through a vacuum has been advanced as a proof of its distinct existence as a material principle; but no perfect vacuum probably can be formed,

and the proof therefore is defective. The phenomena of radiant caloric appears to demonstrate the actual existence of a subtle matter projected in right lines from heated bodies, capable of exciting temperature, and this would afford a conclusive proof of its materiality, were it unequivocally established that these phenomena are wholly independent of the air; but on this point the speculations of Mr Leslie leave some doubt. The existence of calorific rays in the solar beam might be considered as affording similar evidence; but the degree of uncertainty under which the fact still remains with regard to this, leaves an equal uncertainty as to the force of the conclusion. Tho' the hypothesis, therefore, of the materiality of caloric, is superior in its adaptation to the phenomena to that which assigns the production of these phenomena to motion of the particles of matter, it can scarcely perhaps be considered as fully established.

It may be added, that those who have denied the materiality of this power, have limited the discussion, by embracing the hypothesis of Bacon, that the heated state of bodies arises from vibration of their particles,—an hypothesis which gives no adequate explanation. But the question need not be considered under this restricted view. Caloric, if its materiality be not admitted, may be considered as a general force producing repulsion; and if we set aside the facts with regard to its apparent radiation, this perhaps would not be the most improbable opinion on the nature of this power. Our knowledge, however, is not sufficiently advanced on this subject, and, in particular, while the relations of caloric to light and to electricity

remain imperfectly developed, and the nature of these agents is unknown, any hypothesis with regard to the former must rest on imperfect grounds.

The question with regard to the materiality of caloric has been attempted to be determined, by discovering if it is subject to gravitation, or has weight. The investigation of this has given rise to very discordant results; some experiments appearing to establish its gravity, others favouring even the opposite conclusion, that it counteracts gravitation, and, communicated to bodies, renders them positively lighter. These differences arise from the difficulties attending the experiments; and from the subtility of this agent, it is not to be expected, even if it were subject to gravitation, that this could be discovered by any apparatus we can employ. We might probably as well attempt to weigh the particles of light. In some of the experiments, accordingly, made with the greatest care, and with the most delicate apparatus, no sensible difference in weight in a body could be discovered when caloric was communicated to it, and when it was withdrawn.

SECT. VIII.—*Of the Sources of Variations of Temperature, and the Applications of these to Practical Chemistry.*

THE tendency of caloric being to diffuse itself over matter, until an equilibrium of temperature is established, this would at length be attained, did no external causes operate by which it is counteracted. Such uniformity of

temperature, however, would be incompatible with the varied operations of nature; it is therefore prevented by certain general arrangements, constant in their action, giving rise to, and bounding that extent of variation which these operations require.

The great source of natural heat is the action of the solar rays. As every part of the earth's surface is not equally, and at all times exposed to this action, inequality of temperature, giving rise to variety of climate, and change of season, is established. The extreme of heat, which might accumulate where the action of the solar rays is most powerful, is preserved within due limits by changes to which the operation of this heat itself gives rise, and which, so perfect is this adjustment, are even rendered subservient to moderating cold, where it might become intense.

These important effects are obtained, principally by changes in the atmosphere, and in the distribution of water. When the surface of the earth is heated, a portion of this heat being communicated to the air incumbent on it, this is expanded, and of course ascends; an ascending current is established, which is supplied by colder and more dense air pressed from every side; the accumulation of heat is retarded, and the warmer air, propelled to colder climates, gradually gives out the heat it had received. The agency of water is scarcely less important. As the temperature is elevated, it evaporates in greater quantity, and in passing into vapour absorbs caloric, from its increasing capacity, without rising in temperature: when the heat diminishes, or the vapour is carried to

colder regions, it is condensed, and this latent caloric is rendered sensible. Where the cold becomes more intense, water is congealed, and in the congelation gives out the large portion of latent caloric peculiar to it in the liquid form: at the return of warmth, the ice is melted, and caloric absorbed. The transitions of seasons are thus moderated, sudden and extreme variations guarded against, and the temperature of the globe is every where preserved more uniform.

The range of natural temperature is comparatively moderate, extending only from a few degrees above 100 of Fahrenheit to about 50 below the commencement of the scale. In tropical climates, the heat in the shade rises occasionally to 110°. In the north of Asia and of America, the cold, in the winter season, is sufficiently intense to freeze quicksilver, and must therefore be lower than —40; the spirit thermometer has been observed to indicate —50, and there is no reason to believe that any natural cold much exceeds this. The medium heat of the globe, and which, at a sufficient depth from the surface, is stationary, is about 50 of Fahrenheit.

The range of temperature as excited by artificial methods is much greater. We cannot indeed exceed greatly the greatest natural cold, the reduction of temperature by the most powerful freezing mixtures not being more than —90, or 122 below the freezing point of water. But our power of exciting heat is less restricted; it has been measured so high as 160° of Wedgwood's pyrometrical scale, or 21,877° of Fahrenheit; and as at this temperature effects were not produced, which can be obtained

from the concentration of the solar rays by a powerful lens or speculum, or by the heat excited by a current of oxygen gas directed on burning charcoal, heats more intense than this are of course under our command.

An important subject in practical chemistry, is that which relates to the processes for obtaining and applying artificial heat and cold. An account of these, and a description of the apparatus adapted to them, concludes the chemical history of caloric.

THE sources of heat are, the Solar rays, Electricity and Galvanism, Condensation, Mechanical action between solids, including Friction and Percussion, and, lastly, Chemical action, to which Combustion belongs.

From the action of the solar rays without concentration, the thermometer is raised to above 100, and when protected from a current of air, even to above 200. When concentrated by a lens or mirror, the heat is of extreme intensity, equal nearly to any that can be excited by artificial arrangement, all the metals and earths nearly being melted by it, and many of them even dissipated in vapour. It admits, however, of very limited application from the quantity of matter on which it can be made to operate.

The electric spark produces heat sufficient to kindle a combustible body, and the discharge from a battery raises the temperature of the matter through which it is transmitted to a degree more or less intense, according to the strength of the discharge. The galvanic discharge, which

is merely a different form of electricity, produces heat still more intense, melting the most refractory of the metals, and causing all of them to burn. These are afterwards to be considered.

The effect of condensation in producing heat is most conspicuous in the compression or rarefaction of elastic fluids, as in these a considerable change of volume can be suddenly produced. By condensing a gas, its temperature is always raised, and by a forcible and rapid condensation, this extends even to the temperature of ignition, a piece of tinder being easily kindled by condensing the air in a metallic tube. In rarefying any elastic fluid, cold is always produced.

Friction and Percussion are well-known sources of heat. Two solid bodies rubbed against each other always become warm, and frequently so much so, that if inflammable they are kindled; the heat excited varies according to the hardness, elasticity, and other qualities of the body; the hardest are not those that are most heated. Of heat from percussion, the spark struck by steel from a flint is a familiar example, in which the temperature is raised to ignition.

Chemical action is perhaps invariably attended with a change of temperature; it is often productive of heat, and in some cases in a state of high intensity. Combustion is an example of this, this process being the combination of one of the aërial ingredients of the atmosphere, oxygen gas, with the combustible body, and the heat produced arising directly from this combination. It is therefore

much regulated by the rapidity with which the combination is effected.

If oxygen gas, in its pure form, be supplied to the combustible matter, the combustion is extremely rapid, and, of course, the heat is intense, and by this method, indeed, we obtain the highest degree of heat which appears to be capable of being excited by artificial arrangements. The oxygen gas is either directed in a stream on ignited charcoal, or a current of it is mingled with a current of an inflammable elastic fluid, hydrogen, and the mixed gases are kindled. By either of these modes, a heat is excited superior to that in the focus of the most powerful burning lens, and almost every substance may be fused or dissipated by it.

In exciting combustion, merely by supplying atmospheric air to the burning body, it is accelerated, and of course the heat is increased by certain arrangements, causing the air to be more freely and rapidly supplied. On this principle, in particular, is founded the construction of furnaces, a kind of apparatus extensively employed in chemical experiments, as applying heat.

The essential parts common to every furnace, are the body or fire place in which the fuel burns, and where the vessel containing the materials to be operated on is placed,—the chimney by which the smoke and heated air escape,—and the ash-pit designed to receive the ashes of the fuel, and by apertures in which air is admitted to regulate the combustion. The advantage from an apparatus of this kind in exciting combustion, is derived from its causing a more rapid circulation of air. The air in the

upper part of the furnace is rarefied by the burning fuel; it therefore ascends by the chimney, and colder air being pressed in beneath, rises through the interstices of the fuel, and produces a rapid combustion. From this it is evident, that the higher the chimney is, (at least to the extent of the air within it not being much cooled,) the more rapid the current of air will be, for the difference will be greater between the specific gravity of the column of heated air, and the corresponding column of the external atmosphere. On this, therefore, principally depends the power of the furnace to produce intensity of heat.

It is necessary, too, to confine the heat and prevent its dissipation. This is accomplished by coating the inner surface with some substance which transmits the heat slowly, as a lute of clay and sand, which likewise serves to defend the furnace, when constructed of metal, from the action of the fire. When fixed, and built of brick, the building is a sufficiently imperfect conductor to confine the heat.

A very convenient general furnace, applicable to most of the operations of chemistry, was contrived by Dr Black. It is represented Plate II. Fig. 11. A is the body of the furnace, of an elliptical form, which contains the fuel, and frequently the substance to be operated on, made of plate-iron, and lined to the thickness of two or three inches, first with a mixture of clay and charcoal, beat into a paste with water, and over this, next to the fuel, with a coating of clay and sand. On the top of the body is fixed an iron-plate, having two apertures, one, *a*, placed over the cavity, and designed to receive an iron-pot with sand, the other

smaller, to which the chimney, B, made of a tube of iron, is fixed. C represents the grate, in a plate of iron which is fixed to the bottom of the body of the furnace, nearly, but not exactly opposite to the larger aperture in the upper plate. D is the ash-pit, the body of the furnace being received into it, and resting on a strong ring round the cavity, at about half an inch deep. In this ash-pit is a door, *b*, turning on hinges, to remove the ashes; and a register, *c*, designed to regulate the admission of air. It is a plate of iron, in which are six apertures, filled with plugs; the size of them increasing in geometrical ratio, so that by opening them singly, or in combination, the supply of air to pass through the fuel, and consequently the heat to be excited in the furnace, can be regulated with precision. The fuel is introduced at the top, but as it cannot easily be supplied this way in the progress of the process going on in the furnace, at least when the sand-pot is used, the furnace is sometimes constructed with a door in the side, though this renders the regulation of the admission of air less perfect. When the furnace is used for fusion, or similar purposes where a sand-pot is not required, the upper aperture is covered with a dome.

In operations on a larger scale, a fixed furnace of brick, and capable of exciting an intense heat, is required. Fig. 12. represents the usual form of a melting furnace of this kind, the structure of which is obvious from the figure. A is the cavity of the furnace, terminating by a passage in the chimney B, which is raised to the requisite height. At C is an aperture covered with a plate of iron, or of fire-brick, through which fuel is introduced. On the grate, D,

is placed a covered crucible, on a pedestal of baked clay, and in the passage of the chimney, at *a*, a muffle is sometimes placed; E is the ash-pit, through which the air is admitted to the fuel.

When solid substances are to be exposed to these intense heats to fuse them, or to favour their mutual chemical action, crucibles are the vessels generally employed, for experimental purposes. The Hessian crucible, as it is named, is a species of earthen-ware or baked clay, which stands the most intense heat without fusing; the only disadvantage attending it is, that it is liable to be cracked by very sudden alterations of temperature. The black-lead crucibles, made of plumbago and clay baked, are not liable to this, and are, therefore, often used, especially in fusing metals; from a number of saline substances, however, they suffer corrosion. The usual form is represented Fig. 13. Crucibles of platina are sometimes used. Cupels are small cups made of bone-ashes, very porous: they are used principally in refining the more precious metals, which are not oxidated by heat and air, any oxidable metal combined with them soon suffering this change, and the vitrified oxide being absorbed by the cupel. They are placed under an arched earthen vessel, open at the end, named a Muffle, Fig. 14. by which, while the fuel is excluded, the air which is necessary in the process is freely admitted.

In applying a more moderate and equable heat to favour chemical action, the medium of sand, forming the Sand Bath, is generally employed, and glass vessels named Matrasses or Cucurbits are used. The cucurbit is represented, with the alembic, Pl. III. Fig. 18. as the ap-

paratus which is used in sublimation. The matrass is represented Fig. 9. Pl. II.: from being blown thin and equable, it sustains alternations of temperature with less risk of breaking, and from the length of its neck any vapour which is formed is condensed and falls back.

A convenient method of applying heat from combustion, where it is not necessary that it should be very intense, is by the Lamp-furnace. A lamp with a concentric wick, and internal supply of air, on the principle of Argand's, affords a heat which has the advantage of being easily regulated; the elevation or depression of the wick, and the distance at which it may be placed from the body designed to be heated, allowing the application of various degrees of heat, and their speedy change. By having a double circular wick, the heat is rendered more powerful, at least three times more so than when the lamp with a single wick is used.

The lamp is sometimes attached to an iron or brass rod, on which it slides, and to which are attached rings of different diameters, to support a retort or matrass above the flame, as is represented Pl. I. Fig. 6.

A mode of applying a very strong heat at a small point, is that by the Blow-pipe. This instrument is a conical tube, with a small aperture at its narrow extremity, and having towards that extremity a moderate curvature. It is made of brass, or of glass. By blowing through this tube on the flame of a candle or lamp, in a horizontal direction, the flame is urged in a conical form, and at the extremity of it, or rather at the extremity of an internal blue flame, which is surrounded by one of white light, a

heat comparatively intense is excited. It is used by the chemist and mineralogist to ascertain the fusibilities of bodies, and by the artists, in enamelling and in working on glass, which is melted by it, so as to be capable of being moulded into any shape, or blow into vessels of a small size.

The facility of blowing through the blow-pipe, so as to keep up a constant stream of air, is not easily acquired, and it is fatiguing to continue it for any length of time. Different contrivances have been had recourse to, to obviate this inconvenience. The instrument is sometimes connected by a flexible tube with double bellows worked by the foot, by which a uniform stream of air is forced through the tube. The vapour of spirit of wine has been applied to the same purpose: a quantity of spirit being put into a small vessel, which is heated over the flame of a lamp; and the vapour conducted through a curved tube is directed on the flame of a candle, or that of a wick placed in a different part of the same tin lamp as that by which the spirit is heated. A safety valve is adapted to the vessel containing the spirit, to render the flame more regular.

The sources of Cold are Rarefaction, Evaporation, and Chemical Action.

The operation of the first is scarcely conspicuous but in elastic substances, as in these only can the volume be suddenly changed to any considerable extent. When a gas is rarefied by removing pressure from it, its temperature always falls, and the more sudden and great the

rarefaction is, the cold produced is greater. By allowing air, previously compressed, to expand suddenly, the temperature is reduced below 32°.

In the transition of substances to the aërial form, an augmentation of capacity always happens, whence an absorption of caloric follows. Evaporation, therefore, is always attended with cold, and is greater, according as the liquid passes more quickly into the aërial form, or as this is accelerated by circumstances. Thus, the bulb of a thermometer being moistened with water, and the evaporation being promoted by directing a current of air on it, the temperature falls 5 degrees, with alkohol under the same circumstances 12 degrees, and with sulphuric ether 30 degrees. On removing the pressure of the atmosphere, the evaporation is of course more rapid, and hence the cold is greater.

Chemical action is a source of much more intense cold, by the rapid change of form to which it gives rise, solid substances, by combining, passing into the liquid form, and this being attended with enlargement of capacity.

The most simple example of this, is in the solution of a salt in water, which is always attended with a fall of temperature, in some cases to the extent of 20, 30, or 40 degrees. When mixtures of salts are dissolved, the reduction is still greater, and these form what are usually named Freezing Mixtures. Equal parts of muriate of ammonia, and of nitre in powder, added to water in the proportion of 5 parts to 8, reduce the temperature from 50° to 11°, and this forms one of the most economical of

these mixtures, as the solid matter recovered by evaporation, and dried, answers equally well as before.

By dissolving salts in acids more or less diluted, greater degrees of cold are obtained. Sulphate of soda, added to sulphuric acid, previously diluted with an equal weight of water, depresses the temperature from 50° to 5°. Mixtures of salts cause a still greater depression. From phosphate of soda, and nitrate of ammonia, added to diluted nitric acid, a reduction is obtained from 50 to —21.

The cold from similar actions exerted between these substances, and ice or snow, is still more intense; as in the change which results, the absorption of caloric from the liquefaction of the ice is added to that from the solution of the saline matter. Acids, in a certain state of dilution, poured on snow or ice, reduce the temperature to 10, 20, or 30 degrees below the freezing point of water. Solid salts mixed with snow are often equally powerful. A mixture of common salt and snow, afforded Fahrenheit the temperature at which he commenced his scale. A mixture of dry potash and snow reduces the temperature to —53°, and a mixture of muriate of lime and snow to —56°.

From the application of these freezing mixtures, the effects of intense cold on a number of substances have been ascertained. Quicksilver is easily rendered solid; the most ductile of the metals lose their ductility; liquids that resist freezing most powerfully, as wines, brandy, ether, and nitrous acid, are congealed; and some of the gases that appear permanent, as ammonia, and oxy-muriatic acid gas, have been brought to the liquid form. This

process of artificial refrigeration requires to be conducted with attention to several circumstances. The solid salts ought to be recently crystallized, dry, and reduced to fine powder, the due proportions observed, the materials accurately mixed, the vessel employed an imperfect conductor, the air excluded as much as possible, and, to attain extreme cold, the materials must be previously cooled, taking care only not to cool them below that temperature at which they can act on each other.

The theory of the action of freezing mixtures ultimately rests on the principle, that the reduction of temperature arises from the augmentation of capacity, produced by the rapid liquefaction of the solid ingredients. There are some general facts, however, connected with this of considerable interest, particularly as enabling us to point out what substances are best fitted by their mutual action to produce cold, what degree of cold may be expected from their mixture, what will be the maximum of refrigeration, and what the best proportions of the materials.

It is obvious, that those substances will produce the greatest cold, which, by their mutual action, produce the most rapid solution,—which, during that solution, suffer the greatest augmentation of capacity,—and which form a compound that at low temperatures remains liquid. There is perhaps no individual mixture in which these circumstances are present to the greatest extent; yet the knowledge of them enables us to point out the respective powers of the mixtures usually employed.

Thus, in the solution of a salt in water, there is merely the gradual transition of the solid to the fluid form; hence

the cold produced is not considerable. When two salts are mingled together, these, by their reciprocal action, both accelerate the solution of each other, and enable a given quantity of water to dissolve a greater quantity: as more solid matter, therefore, passes to the liquid state, and does so more quickly, a greater portion of caloric is absorbed in a given time, and a greater degree of cold is produced. The attraction of acids to water, or rather to the solid particles of water, is strong, and their mutual action energetic; ice too is a substance which, in its transition to fluidity, suffers a large augmentation of capacity; hence it may be concluded, what experiment proves to be just, that from the action of acids on snow or ice, a great degree of cold will arise. Lastly, in the mixture of two solid substances, which by their mutual action pass to fluidity, the comparative enlargement of capacity must be greater, and a greater diminution of temperature produced, though this is in some measure limited by the greater slowness with which two solids act on each other.

Another principle is to be attended to, which in these mixtures modifies the quantity of caloric that is absorbed from the liquefaction. Although the indirect consequence of the chemical action between the substances mixed is absorption of caloric, in consequence of the liquefaction it occasions, yet its direct tendency is to evolve caloric, by the increase of density which chemical action, independent of change of form, always occasions. Hence two effects result from the mutual action of the ingredients of freezing mixtures,—evolution of caloric, as the immediate result of the combination, and absorption of caloric, as the

result of the liquefaction to which the combination gives rise; and the ultimate effect is compounded of these, or the actual change of temperature is only the excess of the one over the other. This is generally cold, but the reverse sometimes happens, as in pouring a concentrated acid on snow, or dissolving solid potash in water; and where cold is produced, it is always lessened by this cause. It is therefore sometimes advantageous to diminish the energy of the more active substance by previous dilution, as in employing the acids; and in all cases there is a certain state of concentration of the materials, and a certain proportion of them, from which the greatest cold will be obtained.

Lastly, it is to be remarked, that we do not obtain the reduction of temperature to the lowest point in the thermometrical scale from those mixtures which, during their mutual action, absorb most caloric. If we take two freezing mixtures at 32°, the one muriate of lime and snow, the other diluted sulphuric acid and snow, the former will produce more cold than the latter; it will sink the thermometer to —40° or —50°, while the other will sink it to not more than—25°. But we may reach a lower point in the scale of temperature, by successive application of diluted sulphuric acid and snow, than we can do by muriate of lime and snow; for, past a certain temperature, the latter mixture does not liquefy, but, on the contrary, were it liquid would become solid, while the former remains liquid at lower temperatures than this. If we cool, therefore, previous to mixture, muriate of lime and snow to —73°, no advantage is gained; we even rather diminish their mu-

tual action, by adding to the cohesion of each. But by previously cooling diluted sulphuric acid and snow, an important advantage is gained; the same limit is not placed to their mutual action, and the lower the temperature is reduced, the lower will the temperature be that results from that action, down to the point at which the liquid formed by the action of the acid on the snow would congeal.

This furnishes us therefore with the general rule, that the temperature can never be reduced by a freezing mixture beyond that point at which the liquid combination resulting from that mixture congeals or crystallizes, and must indeed always be a degree or two above it. It also, in some measure, determines the proportions in which the substances should be mixed together; those being best, in which the action shall be most rapid, without being too energetic to evolve heat from the combination, and in which the resulting solution is of that strength, that is least liable to congeal or crystallize.

In the following Table, without including all the mixtures that have been employed, I have inserted, from the experiments of Lowitz and Walker, a few, which are either economical, easily managed, or capable of producing very intense colds.

TABLE OF FREEZING MIXTURES.

	Temperature reduced,
Muriate of ammonia, 5 parts, nitrate of potash 5, water 16,	from 50° to 10°
Muriate of ammonia, 5 parts, nitrate of potash 5, sulphate of soda 8, water 16,	50 to 4
Sulphate of soda 8, muriatic acid 5,	50 to 0
Sulphate of soda 5, sulphuric acid diluted with an equal weight of water 4 parts,	50 to 3
Sulphate of soda 6, muriate of ammonia 4, nitre 2, diluted nitric acid 4,	50 to–10
Sulphate of soda 6, nitrate of ammonia 5, diluted nitric acid 4,	50 to–14
Muriate of soda 1, snow 2 parts,	32 to –5
Nitric acid diluted, snow	32 to–10
Concentrated sulphuric acid, snow,	32 to–10½
Muriate of soda 2, muriate of ammonia 1, snow 5,	32 to–12
Carbonate of potash, snow,	32 to–17
Muriate of soda 10, nitrate of potash 5, snow 24,	32 to–18
Sulphuric acid diluted with one-half its weight of water, 2 parts, snow 3 parts,	32 to–23
Concentrated muriatic acid 5, snow 8,	32 to–27
Concentrated nitrous acid 4, snow 7,	32 to–30
Muriate of lime 5, snow 4,	32 to–40
——————— 3, —— 2,	32 to–50
——————— 5, —— 3,	32 to–53
Potash 4, snow 3,	32 to–51
Muriate of lime 2, snow 1,	0 to–66
——————— 3, snow 1,	–40 to–73
Sulphuric acid diluted with half its weight water 10, snow 8,	–68 to–91

These observations on the range of temperature, natural or artificial, may be concluded with a Table, exhibiting the principal points that have been marked in the scale of heat.

	Wedg.	Fahren.
Extremity of the scale of Wedgwood's thermometer - - - -	240°	32277°
Greatest heat of an air furnace, which neither melted nor softened Nankeen porcelain	160	21877
Chinese porcelain softened, best sort -	156	21357
Cast iron thoroughly melted - -	150	20577
Hessian crucible melted - -	150	20577
Cast iron begins to melt - -	130	17977
Greatest heat of a smith's forge -	125	17327
Flint glass furnace (strongest heat) -	114	15897
Welding heat of iron, greatest -	95	13427
Welding heat of iron, least - -	90	12777
Fine gold melts - - -	32	5237
Settling heat of flint glass - -	29	4847
Fine silver melts - - -	28	4717
Swedish copper melts - -	27	4587
Brass melts - - -	21	3807
Red-heat fully visible in day-light -	0	1077
Iron red-hot in the twilight - -		884
Heat of a common fire - - -		790
Iron bright red in the dark - -		752
Zinc melts - - - -		700
Quicksilver boils - -		672
Lowest ignition of iron in the dark - -		635
Linseed oil boils - - -		600

	Fahren.
Lead melts - - - -	594°
Sulphuric acid boils - - -	590
Sulphur burns - - -	——
Phosphorus boils - - -	554
Bismuth melts - - - -	476
Tin melts - - - -	442
Nitric acid boils - - -	242
Sulphur melts - - - -	226
Water boils (the barometer being at 30 inches)	212
Alkohol boils - - - -	174
Phosphorus melts - - - -	100
Ether boils - - - -	98
Heat of the human blood - -	98
Medium temperature of the globe - -	50
Ice melts - - - -	32
Strong wines freeze at about - -	20
A mixture of alkohol and water, equal parts, freezes	—7
A mixture of 2 parts of alkohol and 1 of water freezes	—11
Melting point of quicksilver - -	—39
Liquid ammonia crystallizes - -	—42
Nitric acid, spec. gr. about 1.42, freezes -	—45
Sulphuric ether congeals - -	—47
Natural temperature observed at Hudson's Bay -	—50
Ammoniacal gas condenses into a liquid -	—54
Cold produced from diluted sulphuric acid and snow, the materials being at the temperature of —57 -	—78½
Greatest artificial cold yet measured (Walker) -	—91

CHAP. II.

OF LIGHT.

THE materiality of Light, and its insulated existence, are sufficiently demonstrated. Its emission from bodies, its motion even to the most distant regions of space independent of any medium, the changes which may be produced in that motion by reflection and inflection, and the chemical effects it produces, are proofs of this material existence, free from all doubt. We cannot easily, however, trace the combinations of light: we observe only its evolution and absorption, and the effects arising from these, without being able to discover how far it influences the constitution of bodies in which it exists, or to what extent it is liable to the laws of chemical attraction. Its chemical history, therefore, falls to be considered under a point of view nearly the same as that under which caloric is regarded. And with that power it may justly be associated as a repulsive agent, the particles of light being mutually repellent, and operating perhaps as much in producing chemical change by the repulsion they communicate, as by the affinities they exert.

Light has been regarded as consisting of particles of extreme minuteness, projected from luminous bodies, and moving in right lines with the utmost velocity. It has also been considered as a continuous fluid of perfect elasticity and extreme tenuity, diffused through space, in

which vibrations are excited by luminous bodies, so as to produce its peculiar phenomena. The former opinion has been more generally received, as better adapted than the other to the explanation of the physical affections and relations of light; and it appears to be more directly established by the chemical agencies of this power,—its absorption by bodies, and its subsequent evolution. If it be admitted, the minuteness of the particles of light must be extremely great, beyond even what the imagination can clearly conceive, as is evident from the velocity of their motion, and their not being interrupted, though moving in space through which innumerable rays are constantly projected.

The particles of light are mutually repellent. So perfect is its elasticity, that it is reflected from a body at an angle equal to the angle of its incidence. It is subject to the attraction exerted between masses of matter, as is proved by the inflection it suffers in passing near to any body, or in passing obliquely from one medium into another, giving rise to its refraction.

A ray of light is not homogeneous, but consists of particles suffering refraction in different degrees, and hence capable of being separated. These excite the sensation of vision under different modifications, giving rise to different colours, and produce different chemical effects. An entire ray of light is thus, by transmission through a triangular glass prism, divided into seven rays, the red, orange, yellow, green, blue, indigo and violet, the red being the least refrangible, and therefore falling on a space least distant from that on which the undivided ray would have im-

pinged, had its direction not been changed; the violet being the most refrangible, and falling therefore on a space most distant from this; the others being arranged between these; the whole forming the prismatic spectrum. In this the different coloured rays occupy unequal spaces, and their limits are not perfectly defined.

Of these coloured rays some have been supposed primary, the others being formed by their intermixture. Each, indeed, suffers no change by farther refraction, but this is not to be expected even on this hypothesis, since, if any of them is composed of two kinds of rays, these must be of the same refrangibility, as it is only from this coincidence that they could have remained associated after the first refraction. The red, yellow, and blue, have been supposed primary, as they give rise to the other colours by their intermixture: this distinction has also been assigned to the red, green, and violet, the intermediate colours in the spectrum being formed by the union of these two and two, and white light being obtained by combining the three. The differences in the properties of the coloured rays have been supposed by some to depend on the different magnitudes of their particles, by others on the different velocities with which they move,—suppositions which, however they may be adapted to the physical relations of these rays, scarcely explain the differences in their chemical powers.

Light is differently affected by different bodies. It passes through some with little interruption; by others it is reflected; some reflect one ray retaining the others,—an effect giving rise to the colours which bodies exhibit;

there are, lastly, some in which the light is absorbed, and is lost by numerous reflections and refractions.

Light forms, too, a more intimate union with bodies, of which there appear to be different degrees. By some it is absorbed, and is again slowly emitted without any sensible change: in others it occasions alterations of temperature, or of composition, acting as an important chemical power.

The property which has been named Phosphorescence, appears to depend on the first of these kinds of combinations. There are a number of substances which, when exposed to light, appear luminous when removed from it, and continue so for a longer or shorter time. These are named Solar Phosphori, and the luminous appearance in them appears to arise from the light being imbibed, and again slowly emitted.

This property is conspicuous in a number of natural substances, particularly in earthy minerals, as the gems, marble, heavy spar, fluor spar, and others; and also in bodies belonging to the vegetable and animal kingdoms, as in sugar, paper, the shells of marine animals, &c. Solar phosphori can be prepared by artificial processes still more powerful. The Bolognian phosphorus, in which the property was first observed, is prepared from sulphate of barytes made into a paste with mucilage, and calcined in contact with ignited charcoal. Canton's phosphorus, which is still more powerful, is formed from calcined oyster shells, mixed with sulphur, and exposed to the heat of ignition in a crucible for an hour.

There is much diversity in the degree of phosphorescence. Some, even after exposure to solar light, shine so feebly, that the eye requires to be rendered sensible by previous darkness to perceive it. Others are illuminated by the mere light of day; and some become phosphorescent when exposed to the light of a lamp. Some are rendered luminous by an electrical discharge. The light emitted is not always white; it is frequently yellow or red, and some exhibit the prismatic colours.

Temperature has a marked effect on the emission of light by these bodies. When they are shining, the luminous appearance ceases if they are exposed to the cold of a freezing mixture. It becomes more vivid by applying heat; and if it has ceased, it may be renewed by applying a stronger heat, so that a piece which has been for some time quite dark, may be made to shine. When the phosphorescence, however, has been excited by heat, it ceases proportionally sooner, and is not renewed but by exposure again to light.

This property is quite independent of the action of the air; a phosphorescent substance shining clearly when inclosed in a mass of glass.

The phenomena of solar phosphorescence appear to lead to the conclusion, that light is absorbed by the phosphorescent body, and is again emitted, this emission being promoted by the repulsive agency of heat. There is an objection, however, to this in the fact, which appears to be sufficiently established, that, in exposing the phosphorescent body to a particular coloured ray, it is not this coloured light it emits, but merely the light which usually

proceeds from it; one which shines with a white light continuing to do so, whatever ray of the spectrum it has been exposed to; or one which usually exhibits the prismatic colours when rendered luminous, still doing so whether it has been submitted to white light, or to the coloured light of any individual ray. These facts are singular, and not easily explained on any theory; but it is not impossible that one species of coloured light may be capable of being converted into the others,—a supposition which would, in some measure, reconcile them with the obvious theory of phosphorescence.

Another species of phosphorescence is that excited by heat, independent of any previous exposure to light, and incapable of being renewed. It is exhibited particularly by fluor spar, by several of the gems, and by a number of earthy fossils, the luminous appearance being more or less vivid when heat is applied. The light emitted is often coloured; that from fluor spar is purple; in some the luminous appearance is momentary, in others it continues longer; it is equally, with the former, independent of any action of the air.

Phosphorescence, apparently similar to this, is excited by attrition; two pieces of quartz, for example, appearing luminous in the dark when rubbed against each other, and other fossils shining even from very slight friction. From some the light is colourless, from others coloured: its production is independent of any action of the air, as it is equally bright under water; it is not accompanied with any signs of electrical excitation. The attrition might be supposed to excite the light by the heat it may

produce; but the very slight friction that is often sufficient to produce the luminous appearance, that, for example, by rubbing a feather on the surface, is unfavourable to this opinion: there are fossils, too, rendered phosphorescent by friction and not by heat, and *vice versa*; and in those which are phosphorescent from both causes, if the luminous appearance has been excited by heat until it cease to appear, it may be produced anew by attrition.

A kind of phosphorescence, different from any of the preceding varieties, is that exhibited by animal matter. Marine animals are remarkable for this property; almost all the species of sea fish becoming luminous after they have been removed for some time from the water, and continuing to shine for some days. The same appearance has been occasionally observed from the flesh of quadrupeds. It does not appear until the animal has been for some time deprived of life, but it is always apparent before there are any signs of putrefaction, and it ceases when that process is fully established.

The most important fact with regard to this species of phosphorescence is, that the matter having the luminous quality can be extracted in a state of solution. If the substance of any marine animal in the phosphorescent state be macerated in a saline solution, as that of sea-salt, or indeed any other neutral salt of a certain strength, a lucid ring soon appears at the surface of the liquid, and the whole becomes luminous when agitated; this continues for several days, becoming gradually more faint until it is extinguished. Fresh water is incapable of extracting this luminous matter; the luminous appearance in salt water

is extinguished by acids, alkalis, ardent spirit, and other substances. A certain degree, too, of saline impregnation is necessary to its appearance; for it is suspended by a solution either too dilute or too concentrated, being revived in this case when the proper state of concentration is restored.

This phosphorescence is augmented by agitation: it is impaired and even extinguished by cold, but is revived by heat: if the heat, however, be too high, such as that of boiling water, it is irrecoverably extinguished. Exclusion from the atmosphere prevents its appearance, and a number of elastic fluids not only prevent it from appearing, but extinguish it when it has been produced. It is not brighter, however, in oxygen gas than in atmospheric air; neither is it accompanied with any sensible heat.

The light from rotten wood appears to be of a similar kind, observing, in its production and extinction, very nearly the same relations.

Light is emitted from certain insects, as from the glow-worm, or the lantern-fly: the light is variable, being at one moment brilliant, at another faint. The luminous appearance depends on a peculiar secretion, and may even be obtained from its receptacle by compression; it continues to shine, too, for some time after the death of the animal. It had been observed, that the light of the glow-worm becomes more vivid when it is placed in oxygen gas, which gave rise to the suspicion of its being produced by the chemical action of oxygen. The gas, however, appears to act rather by exciting the secretion, for the oxygen is not impaired in purity; and the luminous appear-

ance is obtained when the animal is under water. This species of phosphorescence, like that from marine animal matter, is extinguished by hydrogen gas, carbonic acid gas, and various other elastic fluids, reviving, however, on the admission of atmospheric air.

An important part of the chemical history of light relates to its power of elevating temperature. The solar rays are the great source of natural heat; and when concentrated, excite a very intense heat.

Different kinds of matter are unequally heated by solar light; through transparent bodies the rays passing with little interruption, the temperature is not so much raised as in those which are opaque, and those which are white are less heated than those of a darker shade.

A still more important fact connected with this property is, that the different coloured rays of light have different heating powers. Hutton observed, that the red ray of light has more heating power than white light. Rochon found that an air thermometer, exposed successively to the action of the different coloured rays, separated by a prism, rose higher as it was moved from the violet to the red, the difference in the two extremes being nearly 8 to 1. Herschel and Englefield have demonstrated the same general fact, and shewn the relative heating powers of the coloured rays with more precision. The rise of a delicate mercurial thermometer placed in the focus of a lens, and exposed to the coloured rays obtained by a prism successively, is shewn in the following table, as established by the experiments of Englefield.

In the blue ray	in 3′	from	55° to 56°
In the green ray	in 3	from	54 to 58
In the yellow ray	in 3	from	56 to 62
In the full red ray	in $2\frac{1}{2}$	from	56 to 72
In the confines of the red	$2\frac{1}{2}$	from	58 to $73\frac{1}{2}$
Quite out of visible light	$2\frac{1}{2}$	from	61 to 79

From the last number in the table it will be perceived, not only that the fact is proved of the different coloured rays having different heating powers, but that the not less important result is established, that there exist in the solar beam invisible rays which are powerful in producing heat, these being accumulated beyond the red ray when the entire beam has been decomposed by the prism, and being, of course, less refrangible than the red ray. This had been previously shewn by the experiments of Herschel. Exposing a thermometer to the different rays of the prismatic spectrum, each ray being allowed to pass successively through a piece of pasteboard with a slit in it, so as to exclude the others, he found not only that the heat increased progressively from the violet to the red ray, but that when the aperture in the pasteboard was brought to coincide with the space beyond the red ray, the heat continued: it was even greater at the distance of half an inch than in the red ray itself, and is here at its maximum; as is apparent, also, from the numbers in Englefield's table: at the distance of an inch, the rise of the thermometer amounted to $5\frac{1}{4}°$, being 7 in the red ray, and the heating power was sensible at the distance even of an inch and a half. Beyond the violet ray there is no sensible heat.

Admitting the accuracy of these experiments, it is established, that in the solar rays, there are invisible calorific rays, as well as visible rays of light. Now this being proved, the hypothesis, it is evident, may be proposed as not improbable, that the apparent heating power of the visible rays of light is not a property belonging to them, but depends on the presence of calorific rays associated with them. The entire beam of visible light is not homogeneous, but consists of rays, which, being of unequal refrangibility, are capable of being separated, forming, when thus refracted, the visible or coloured spectrum. But the calorific matter in the solar beam, it is equally probable *à priori*, may not be homogeneous, but like light may consist of rays of different refrangibility. If so, these rays will also be separated by the prism, and an invisible calorific spectrum be formed, the rays composing which may differ in heating, as the rays of light differ in illuminating power. If this happen, the one spectrum will be in some measure blended with the other, and thus the visible rays of light will appear to have different degrees of heating power, though in themselves they may have no power whatever to produce heat.

Herschel endeavoured to establish this conclusion, by experiments resting on the following assumption: Taking the illuminating power as the property characteristic of visible light, if the heating power of any ray be a property belonging to it, and not depending on any calorific ray associated with it, it seems obvious, that when the coloured ray is transmitted through a certain medium, as, for example, through glass, its illuminating and heating powers

must be diminished exactly in the same proportion. It is not to be expected, that it will pass through without a certain degree of interruption; but it may be presumed, and appears indeed to be a necessary inference, that if both properties depend on the same matter, they must be diminished to the same extent, while, if the illuminating power depends on one kind of ray, the heating power on another, it is possible, *à priori*, and indeed to be expected, that these will be unequally intercepted, and of course the powers will be unequally impaired.

To ascertain the fact with regard to this, a very extensive series of experiments was executed by Herschel, and the general result established, that the two powers, that of illumination, and that of heat, are very unequally impaired by transmission of light, either entire, or in the state of the different coloured rays through transparent media, as different liquids, or glass of different colours. In some the heating power was considerably more impaired than the illuminating power, and in others the reverse was the case.

It appears to follow, therefore, that the two properties do not depend on the same agent: the illumination depends on rays of light, the heat on calorific rays; and in any coloured ray the two properties appear, merely because from the correspondence in the order of refrangibility, certain of the calorific rays are associated with certain of the visible rays of light. Herschel has pointed out some other discordant results in comparing these, which strengthen the conclusion; the interruption, for example, of the rays of heat becoming less, as the experiment of its transmission

is continued; while this does not happen with regard to light: and the effect of rough surfaces in scattering the rays of light being much greater than it is on the rays of heat.

The agency of light in producing chemical decomposition still remains to be stated. This may, in a great measure, be generalized; all the changes of this nature produced by its action arising from the separation of the principle, oxygen, from states of combination. And as this element enters into the constitution of an extensive series of compounds, a number of substances are changed by light exerting its de-oxidating power. Thus, several of the acids are decomposed. If nitric acid, which is colourless, be exposed to the rays of the sun, it becomes of a yellow colour, and oxygen is disengaged from it. Oxymuriatic acid, under a similar exposure, likewise yields oxygen, either the oxygen peculiar to it, or derived from the water. A number of compounds of metals with oxygen, either alone, or in combination with acids forming metallic salts, undergo a similar decomposition: in some of them this is partial; in others of them, as in the salts of gold or silver, it is complete, so that the metal returns to its metallic form. Some of these compounds are extremely sensible to the chemical agency of light: muriate of silver, for example, is darkened in its colour by the mere light of day, without direct exposure to the rays of the sun. The changes of metallic pigments from exposure, appear in general to arise from this action of light.

The process of bleaching, too, appears to depend chiefly on the chemical power of light, the colouring matter of

the vegetable fibre apparently receiving oxygen from the decomposition by light of the water with which it is moistened; and the new method of bleaching which has been substituted, owes its superiority principally to oxygen being afforded to the colouring matter in a more condensed state.

The changes which growing vegetables suffer under exposure to the solar light, display its power in modifying, even by its chemical agency, the processes of animated nature. If light is excluded, or very partially supplied, they are in general feeble, of a pale colour, and do not afford their proper products fully formed: if it is freely admitted, they soon acquire a green colour and their natural vigour: the plants which grow under a clear sky and an intense solar light, are even in general more aromatic, and afford more rich and elaborated juices than those which grow under the opposite circumstances. With these results we can connect the usual chemical change from the action of light, oxygen being exhaled from plants while under exposure to the rays of the sun. Even on animals light perhaps exerts its chemical power: those who are natives of the arctic regions, being, like vegetables secluded from light, usually of a pale or white colour, while those who inhabit tropical countries are marked by deep or brilliant hues.

It might be supposed that these chemical effects depend not on any peculiar action of light, but arise from its power of exciting heat; some of them, at least, being produced by an elevation of temperature. An experiment of Scheele's appears to set aside this supposition; nitric acid, exposed to

the sun's rays in a phial painted black, not undergoing the usual change it does from their action, though its temperature must have been more elevated than if it had been exposed in a clear phial. Berthollet also found, that the oxymuriatic acid, exposed to the light in a phial covered with black paper, did not suffer its usual change, though it must have been at least equally heated. But these experiments are not perfectly conclusive; for we cannot estimate correctly the heat produced by the solar rays from the elevation of temperature in the entire mass of matter exposed to them, as this may be moderate, while it may be intense in the minute points on which the rays impinge, and at these points it may, from its intensity, give rise to the decompositions which are produced. The hypothesis, however, that light acts in producing these decompositions by the heat it excites, is refuted by the fact to be immediately stated, that those rays most powerful in exciting heat, are least powerful in giving rise to chemical changes.

The comparative powers of the different coloured rays in producing chemical decomposition, were submitted to experiment by the illustrious Scheele, muriate of silver, the substance which is so rapidly affected by light, being exposed to their action; it became sooner black, he observed, in the violet ray than in any of the others. Sennebier ascertained the differences more minutely. The shade produced in the muriate of silver by exposure to the violet ray for 15 seconds, required for its production, exposure to the indigo ray 23 seconds; to the blue 29; the green 37; the yellow 5½ minutes; the orange 12 mi-

nutes; and the red not less than 20 minutes. The blue ray too is superior to the others in exciting phosphorescence.

The discovery of the existence of invisible calorific rays in the solar beam might suggest the conclusion, that there may also exist in it invisible chemical rays, to which the chemical powers of these visible rays is to be ascribed. Ritter submitted this conjecture to experiment. Placing muriate of silver without the coloured spectrum beyond the violet ray, it was blackened; while, on placing it beyond the red ray at the other extremity, it not only did not suffer this change, but if previously blackened became white. Phosphorus was kindled in the space beyond the red ray, but was extinguished when transferred to that beyond the violet. In the violet ray itself the muriate of silver received a less deep shade than in the space beyond it. Dr Wollaston had nearly about the same time made similar experiments, and with the same results, except that when the muriate of silver had been blackened, however slightly, it did not recover its whiteness from exposure to the red rays.

From these experiments, then, the existence in the solar beam of invisible rays not calorific, but distinguished by their chemical action, and more refrangible than the visible rays of light, is demonstrated. Reasoning by analogy, from the law which has been proved to exist with regard to the calorific rays, it might be concluded, that the matter composing what, for distinction, may be named the Chemical Rays, is not homogeneous, but consists of rays of different refrangibilities; that from this difference

they are spread to a certain extent over the space occupied by the prismatic spectrum, and that, as the calorific effect of the visible rays does not belong to them, but to rays of caloric intermixed with them, so the chemical powers of these rays may not arise, strictly speaking, from the action of light, but from the action of chemical rays blended with the others. It has accordingly been affirmed, that Ritter, by transmitting the coloured rays through different prisms, has separated them from the chemical rays, and thus produced a coloured spectrum without any chemical power. Another interesting experiment performed by him, is that of combining the two species of invisible rays. The power of the chemical rays appeared to predominate in the mixture, and the experiment is an important one, as proving, that from the union of these invisible rays no species of visible light is produced.

From the relation which subsists between light and caloric, it has sometimes been supposed that they are ultimately the same, or are modifications of one matter, light being this matter in a state of rapid projectile motion, and acting as caloric when it becomes quiescent. Though it may be difficult to explain fully the nature of that relation, there seems to be little reason for admitting this hypothesis. The essential properties of light, and particularly its chemical agencies, are very different from those of caloric,—differences which the hypothesis does not explain; more especially taking into consideration the important fact, that these chemical agencies are exerted most powerfully by those rays of light which are least powerful in pro-

ducing heat. And, on the other hand, there is no proof of the assumption, that caloric, in any state of motion, can assume the properties of light.

CHAP. III.

OF ELECTRICITY AND GALVANISM.

The agent on which the phenomena of electricity depend, operates as a chemical power. There is every reason too to conclude, that the galvanic principle is merely electricity under a peculiar form, and in this form its chemical action is still more powerful, and indeed nearly unlimited. The operation of this principle cannot be ascribed to affinities which it exerts, considering it as a material agent; but rather to its action as a general force communicating repulsion or modifying attraction. It is therefore properly classed with light and caloric, and with these it has, besides, very intimate relations, being capable, under peculiar arrangements, of producing the utmost intensity, both of heat and illumination.

Though electricity and galvanism are modifications of the same power, yet, as their mode of excitation is different, and the chemical effects obtained from each are peculiar, they require to be considered apart.

SECT. I.—*Of Electricity.*

CERTAIN bodies submitted to friction exhibit the phenomena denominated Electrical. A dry glass rod, for example, rubbed with a piece of silk, will give sparks of light from its surface, and will attract light bodies and again repel them. These effects, however, are not obtained from the friction of every substance; a metallic rod, for example, does not exhibit them. Hence the distinction of bodies into electric, or those capable of being excited by friction, and non-electric, or those which are incapable of this electrical excitation.

If, when an electric has been excited, a non-electric be applied to it, the signs of electricity in the former instantly cease, while this does not happen from the application of a non-electric of a different kind. Hence the origin of another distinction, that of Conductors, and Non-conductors of Electricity; the former affording a passage to the electrical principle, and carrying it off where it has been accumulated, the latter being impervious to it. Electrics are non-conductors; non-electrics are conductors; glass resinous substances, oils, and sulphur, are the principal substances belonging to the first class; metals, water, and a number of earthy bodies belong to the other.

If an electric, while excited, be supported on a non-conductor, the electricity it gives out is limited. But if a communication be established with the earth by the me-

dium of a conductor, this conveys electricity as long as the exciting cause is applied. If a conductor insulated, that is placed on a non-conductor, be brought nearly in contact with the excited electric, it receives the electricity evolved, and retains it in an accumulated state. On these principles the electrical apparatus is constructed; this consisting of a glass plate or cylinder which revolves against a cushion supported on a glass pillar, but connected with the earth by a metallic chain; and a large metallic tube, named the Prime Conductor, being placed insulated before the plate or cylinder, to receive from it the electricity evolved by the friction.

With regard to the excitation of electricity, a very important distinction still remains to be stated, that of what has been named Positive and Negative Electricity. If a glass rod be rubbed with an woollen cloth, on approaching to it a light body, as a bit of cork, the cork is first attracted, and then repelled; but if a rod of sulphur be excited by friction with the cloth, the cork in the state in which it is repelled by the glass is attracted by the sulphur, and it is repelled by the sulphur when in that state in which it is attracted by the glass. If a pointed conductor, as a needle, be presented to the glass, a round lucid point appears on its extremity in the dark; but if presented to the sulphur, a pencil of rays seem to issue from the needle. And if two bodies in these different electrical states be brought into contact, the electricity in the one appears to destroy that in the other, and the electrical phenomena cease. These two electricities being first obtained, the one from glass, the other from resinous bodies, by

friction, were named the Vitreous and the Resinous, and were regarded as essentially different.

It was discovered, however, that when two electrics are rubbed against each other, the one acquires always the one electricity, the other the other. Thus, in the common electrical machine, when the cushion is insulated, on friction being made it exhibits the resinous, while the glass gives the vitreous electricity. And, by employing different substances to excite friction, or by altering the surface, the same electric may be made to exhibit, either electricity, glass the resinous, and sulphur or sealing-wax the vitreous. Franklin, from these facts, was led to explain the phenomena on a more simple hypothesis,—that there exists only one agent by which they are produced, a fluid highly elastic, or repulsive of its own particles, but attracting and attracted by the particles of other matter; —that in all bodies a portion of this principle is present, and when present, in the proportion natural to each, they exhibit no electrical phenomena; but, if subjected to certain operations, as friction, the equilibrium is disturbed, and the body acquires more, or has less, than its natural proportion. In the former case it is said to be electrified *plus*, and presents the phenomena ascribed to what was called vitreous electricity: in the latter it is said to be electrified *minus*, which corresponds with the state of resinous electricity; and hence, instead of these terms, the phrases Positive and Negative electricity are employed in the Franklinian theory. This hypothesis accorded with the phenomena of electricity, and in particular gave a happy explanation of the discharge of the Leyden phial.

Hence electricians have in general been disposed to prefer it, though it has never been established by any rigorous evidence, nor has the opposite hypothesis been disproved, or shewn to be inconsistent with facts. The principal advantage which the system of Franklin can claim, is its superior simplicity. On the other hand, the phenomena of galvanism prove that the two electricities, whatever may be their nature, exert different chemical agencies; and hence, whatever theory be adopted, it has become more necessary, in their chemical history, to distinguish between them.

Electricity is connected both with light and caloric. In its passage through certain media, it is often highly luminous, and it is capable of exciting intense heat.

Under the form of what is named the Electrical Spark, it produces an elevation of temperature sufficient to kindle inflammable bodies, as spirit of wine. And when discharged in a state of higher intensity from a coated jar, or from an entire battery, a much more intense heat is excited, so as to melt the most refractory substances. Its power of increasing temperature appears in part to depend on the resistance opposed to its conveyance through bodies. Hence, if it is not rapidly accumulated, no sensible heat is produced; as, for example, when the bulb of a thermometer is placed in an insulated metallic plate, and electricity is communicated. But, if the bulb be placed in a less perfect conducting medium, the temperature is raised. Or, if a discharge of given intensity from an electrical battery be transmitted through a metallic wire of considerable thickness, it will not produce much heat.

while, if transmitted through a wire of the same metal of less diameter, an intense heat is excited.

The fusibilities of different bodies, of the different metals for example, estimated from the action of electricity on them, are different from their fusibilities, estimated from the direct communication of caloric, no doubt from the heat excited by electricity, being dependent not merely on the quantity communicated, but on this modified by their relative conducting powers, and perhaps on their elasticities, in consequence of which vibrations are more or less easily established among their particles.

Electricity, from its power of exciting heat, is applied to favour chemical combination: it affords the most convenient mode of promoting by heat the combination of elastic fluids. The apparatus employed is a strong glass tube, Pl. III. Fig. 22. closed at one end, the sides of which, at about the distance of two inches from this extremity, are perforated with small holes, in which are fixed by cement two metallic wires, the extremities of which within the tube are distant one-fourth of an inch. This instrument being filled with water or quicksilver, and inverted, the gases intended to be combined, mixed in the due proportion, are introduced, so as to depress the fluid an inch or more beneath the wires. The electric spark is made to pass from the one wire to the other, by connecting one of them with the conductor of the common electrical machine, and hanging a chain on the other. Or it may be made to pass from a wire inserted in the top of the tube, to the fluid confining the air beneath, as represented Fig. 23. In the mixture of some gases, a single

spark is sufficient to cause the combination to proceed through the whole mixture, the temperature being raised by it sufficiently. In other cases, a stream of sparks requires to be transmitted to produce the combination to any perceptible extent.

By the same agency, electricity is able to effect chemical decomposition. If the spark is taken in a compound gas, it separates its constituent parts; if an interrupted electrical discharge be sent through water, it is attended with the disengagement of a small quantity of elastic fluid, which is a mixture of the two gases which form water. Some solids are decomposed in a similar manner.

The electric fluid is intimately connected with light, and to this some of its chemical effects may probably be attributed. When it passes through the air from one conductor to another, it exhibits a luminous spark; when discharged through a vacuum the most perfect the air-pump can produce, it presents vivid corruscations: these appear even, though more faintly, in the Torricellian vacuum. In transmission through any fluid, if the quantity be not large proportioned to the discharge, it is rendered luminous; or if discharged over the surface of a solid, a brilliant illumination is produced. This electrical light is heterogeneous, or consists of the different refrangible rays. Priestley observed these by a prism; and Morgan has remarked that the electric light may be made to assume different colours according to the medium in which it is taken; sometimes the more refrangible rays being separated, sometimes the less.

The chemical agencies of electricity are as yet but imperfectly developed, and there are a number of facts which prove it to be absorbed or evolved in chemical changes where its influence has scarcely been traced. The electrical phenomena exhibited by the tourmalin shew that electricity is excited, and its different states produced, in some cases merely by variations of temperature. Even its excitation in the electrical machine is promoted by chemical action, as on this appears, in a considerable measure, to depend the effect of the amalgam applied to the rubber, the power of which is greater when it is composed of oxidable metals than of those not so susceptible of oxidation. The experiments of Wilcke and Æpinus shew that in fusion and congelation the different electricities are excited, and the states of *plus* and *minus* produced in the body which has suffered the change of form, and the matter with which it has been in contact during the change: this happens too in the formation and condensation of vapour, and Volta traced it in different cases of chemical action. The observation of such facts becomes more important since the connection of electricity with galvanic phenomena has been established, and that connection itself more clearly demonstrates the importance of electricity as a chemical power.

SECT. II.—*Of Galvanism.*

GALVANISM, there is every reason to believe, is the same principle as electricity. Its effects, however, its mode of production, and the laws which it observes in its action, are so far dissimilar, that it is proper to consider it under a separate section. Our knowledge of this agent is of recent date. Galvani, an Italian physiologist, observed the first striking phenomenon which led to the discovery of the principle which has from him derived its name. He observed it only in its power of affecting the animal system, and it is to Volta that we are principally indebted for the just theory of its production, and the development of its chemical powers. It had been discovered by Galvani, that contractions are excited in the irritable parts of animals, when a communication is established by a metallic arc between the nerve and the muscular fibre; and he concluded, that this is owing to the communication of electricity generated by the animal system. Volta supposed, that the electricity producing the contraction, and producing likewise sensations in sentient organs, is produced not from the living system, but by the action exerted between the metal and the humid animal fibre,—a conclusion which he soon demonstrated, by the discovery that it is evolved by arrangements wholly unconnected with any process of vitality. This discovery also gave a

method of augmenting the galvanic energy, enabled us to investigate its effects with more precision, and led to the discovery of its chemical agency.

The Voltaic arrangement consists of a series of metallic plates arranged in a determinate order, with the interposition of certain humid conductors of electricity. The pile, which Volta principally employed, is constructed by commencing with a plate of silver or copper: on this is placed a plate of another metal, as zinc, and on this a piece of card moistened with a saline solution: this series of copper, zinc, and moistened card, is repeated, preserving alwyas the same order, and when 30 or 50 pieces of each have been accumulated, terminating with a plate of zinc at the top, as represented Fig. 27. Pl. III. Between each pair of plates a certain quantity of electricity is generated; in the whole arrangement, we have the accumulated action; and the effects are proportionally great. The extremities of the series are in different electrical states, that commencing with the copper being negative, that with the zinc positive. Another arrangement similar in principle, employed by Volta, is that which he named *Couronne de Tasses*, represented Fig. 26., consisting of a series of cups, in each of which are placed a plate of zinc, and a plate of silver or copper, surrounded with a solution of salt; the plate of silver in the one cup being connected with that of zinc in the other, and the same order being preserved as in the construction of the pile.

An apparatus, still the same in principle, was invented by Mr Cruickshank, the Galvanic Trough as it is named, which, being possessed of every advantage, is now always

used. It consists, Fig. 28. Plate III. of a hollow box or trough, of hard wood, in the sides of which are cut grooves, at the distance from each other of from $\frac{1}{4}$ to $\frac{1}{2}$ of an inch, according to the width of the box. Plates of two metals, generally of copper and zinc, from 3 to 6 or 8 inches square, are soldered together, and this soldered or double plate is inserted in the first groove of the box, and fixed in it by a cement of resin and wax, so well applied that no liquid can pass through. This is repeated, fixing a double plate in each groove, and taking care that the order in which they are inserted shall not be reversed, but that the copper side shall always be towards one hand, the zinc to the other. The cells or cavities between the grooves are designed to contain the fluid by which the galvanism is excited, or serve the same purpose as the moistened cards in the pile of Volta.

The metals used are generally zinc and copper, and these, on the whole, answer best. The number of plates and their surface is regulated by the purpose to which the trough is to be applied. Different liquids are employed to fill the cavities of the trough, and differ much in power. With water the effect is inconsiderable; with a solution of muriate of soda, or muriate of ammonia, it is greater; it is still more so, though it ceases sooner, with muriatic or nitric acid, largely diluted, and, for different purposes, liquids of peculiar composition and strength are best adapted, as is immediately to be stated.

An improvement has been made in constructing the trough. Instead of soldering the plates together, they are kept detached, and are connected only at the upper edge

by a metallic arc; the cells of the trough are formed by partitions of glass, or the entire trough with its partitions is made of earthen ware. The plates of copper and zinc are introduced, so that the one shall be on one side of the partition, the other on the other, the connecting arc passing over it, and a plate of each metal being thus placed in each cell. This arrangement has the advantage, that both surfaces of each plate being acted on, a greater power is obtained, while, in the former method with the soldered plates, one side of each was lost.

Though arrangements, such as have now been described, are most powerful, there are others productive of galvanism to a certain extent. The action between a single metal and a liquid gives signs of it, extremely feeble, and displayed therefore only in the most delicate test of this power,—the contractions it produces in living irritable parts, but no accumulating series of this kind can be formed. If, however, the metal be acted on at its opposite sides by two different fluids, a galvanic arrangement is formed, the power of which increases by repetition. Even charcoal, in contact with one of its surfaces with one liquid, and at another with a different liquid, forms a weak galvanic power; and one, still weaker, is formed from the contact of different kinds of animal matter. Metallic matter, therefore, is not essential to its production.

The properties of galvanism remain to be stated. It passes through those substances which conduct electricity, though with less facility. Metals conduct it rapidly, but there are other substances which admit of the passage of electricity, which at least partially insulate galvanism; such

in water, or dry animal membrane. Glass is a perfect non-conductor.

Its effects on living animal matter are similar to those of electricity. It excites contractions in irritable parts, and sensations in sentient organs, more or less considerable, according to its intensity.

In its transition from one conductor to another, especially when the conductor is an imperfect one, it produces intense light, as, for example, in bringing into contact the wires from each extremity of the battery, or pieces of charcoal or plumbago in communication with each wire. This light appears to be the result of the accumulation of the galvanism, and not of any combustion, for little of the charcoal is consumed, and it can be made to appear under water and other liquids.

Galvanism is the source of intense heat. If a very fine metallic wire be stretched between metallic rods, connected with each extremity of the galvanic battery, its temperature is raised, and if the distance be not too great, to such an extent as to melt even the most refractory of the metals. Fine metallic leaves, suspended from the one rod, are made to burn when touched with a metallic plate in communication with the other. From this arrangement, even gold and silver enter into vivid combustion, and the least fusible of the earths have been melted.

The most important chemical property of this power is that of producing decomposition. Very soon after the invention of the Voltaic battery, it was observed by Messrs Nicholson and Carslisle, that when wires, connected with the two extremities of the battery, are placed in a portion

of water, a stream of gas arises from each wire, an appearance which they found owing to the decomposition of the water. The subject was immediately prosecuted, and a number of chemical compounds were found to be decomposed in a similar manner. Still more lately, Mr Davy, led by the knowledge of the law which regulates these decompositions, and employing galvanic arrangements of great power, has succeeded in discovering the composition of a number of substances, the nature of which was before unknown to us,—discoveries which have materially changed the aspect of the science, and to the prosecution of which scarcely any limits can at present be assigned, for our power of increasing the galvanic force appears to be nearly unlimited, and with this its energy, in counteracting chemical attraction, appears progressively to increase.

The decompositions produced by galvanism consist in the separation of the elements of a compound from their state of combination, by the attraction uniting them being suspended by the galvanic force. But it was not very obvious how this effect is produced, and a difficulty likewise presented itself with regard to them, from the very singular fact, that the elements of the decomposed compound are not evolved together, but the one appears at the wire connected with the one extremity of the galvanic battery, and the other at the wire connected with the other extremity. To account for this, different hypotheses were proposed, not very satisfactory; at length Messrs Hisinger and Berzelius, from a number of experiments, drew the general conclusion, that by attractive forces

exerted at the galvanic poles, certain elements are brought to the positive side, and others to the negative side of the galvanic series; oxygen and acids being attracted to the former; inflammables, metals, alkalis and earths being attracted to the latter. Hence the decomposition of compounds, consisting of substances belonging to these opposite classes, and the distinct evolution of their elements.

This law has been more clearly developed by Mr Davy's researches. The transfer of the elements of the decomposed compound to a distance, and through interposed matter, has been accurately traced, and a number of interesting facts with regard to it established. The apparatus he employed consisted generally of two vessels of glass, or, as less liable to be acted on, of agate, or of gold, connected by a few fibres of the mineral substance named asbestos, moistened with water (Fig. 24. Pl. III.) The solution of a compound substance, of a salt for example, composed of an acid and an alkali, was put into each vessel thus connected, and they were subjected to the action of the galvanic apparatus, a wire from the positive side being inserted in the one, A, and a wire from the negative side in the other, B. In a short time, when a sufficient power is employed, the principles of the salt are separated, the acid is collected in the one vessel, and the alkali in the other. If the solution of a salt were placed in one vessel, and distilled water in the other, either the acid, or the base of the salt, might be transferred through the communicating substance to the distilled water, according as the solution was connected with the positive or the negative side of the galvanic trough: if with the positive side, the

acid remained, and the base was conveyed to the water; if with the negative side, the reverse was the result. In this way, even metals could be transferred, as silver from nitrate of silver, or insoluble earths, as magnesia, from sulphate of magnesia.

When the vessels themselves were composed of substances susceptible of decomposition, such as earthy compounds, sulphate of lime and others, the same separation of elements was effected, though, from the state of cohesion, more slowly. Even glass was found liable to this decomposition. And such is the force of this agent, that the most minute portion of a substance attracted by either of the wires is collected around it,—a circumstance which has frequently been the source of deception in galvanic experiments, with regard to the apparent formation of new products.

So completely is the matter conveyed by the galvanic influence protected by it, that it may be transmitted through a substance to which it has a chemical affinity, without being retained; as, for example, if a third vessel be interposed between the two, and connected with them in a similar manner by moistened asbestos; if an acid liquor be placed in it, an alkali may be conveyed through this without interruption, and be collected round the negative wire; or *vice versa*, if an alkaline solution be put into the intermediate vessel, an acid may be conveyed through it, and collected at the positive wire. If a strong force of cohesion, however, interfere, the substance is intercepted: thus, sulphuric acid is not transmitted through solutions of barytes or strontites, nor these earths through sulphuric acid. The che-

mical affinities of the conveyed substance are suspended by the galvanic influence; an acid, for example, not reddening a vegetable colour in its progress, but only where it is collected around the positive wire; and an alkali, in like manner, exerting its chemical action only at the negative side.

These decompositions appear to be always complete, or the law of chemical affinity so often observed, that an ingredient of a compound, when separated from a combination, retains a portion of the ingredient with which it had been combined, is counteracted; the transferred substance, Mr Davy found, being perfectly pure.

By these researches, then, the general law is established, that certain substances, oxygen and acids, are attracted by positively electrified metallic surfaces, and repelled by similar surfaces negatively electrified; while inflammable bodies, metals, metallic oxides, alkalis and earths, are attracted by negatively electrified metallic surfaces, and repelled by those which are in a positive state. Hence the phenomena of the decomposition of bodies by galvanism, one of the elements of a compound bring forcibly attracted to the one galvanic pole, the other to the other, while each is at the same time repelled from that side to which the other is attracted. And these attractions and repulsions are exerted at considerable distances, producing therefore the transfer of the bodies acted on through any medium in which they are capable of being diffused. Mr Davy has supposed, that the positive electrical state may be communicated at the one pole to the one element, and the negative electrical state to the other at the opposite pole: this

state may be communicated to the particles of each through the whole column interposed between the two poles, and, in conformity to the law, that bodies similarly electrified repel each other, while those in opposite electrical states attract, the particles of the body in the one state will be attracted to one pole, and repelled from the other; a chain or series of particles will thus be established, moving in this direction, while, for the same reason, the particles of the other element will move in the opposite direction, and the motion of each will continue until the whole is collected around that pole to which it is attracted. Or, perhaps, what is equally probable, the particles receiving the charge at each pole, instead of communicating part of the charge to its contiguous particles, may be at once repelled from that side, and attracted to the other. In atmospheric air, we know that bodies, rendered positively or negatively electrical, are attracted and repelled at considerable distances. From the low state of intensity in which electricity exists in galvanic arrangements, water is a medium with regard to it very nearly as atmospheric air is to electricity evolved in the common electrical apparatus, and it may therefore allow electric attractions and repulsions to operate in a similar manner.

Mr Davy has suggested the hypothesis, that even chemical affinity itself may be a modification of electrical energy. Bodies in the same electrical states repel each other; but when in opposite electrical states, they mutually attract. It is conceivable, that some kinds of matter may be naturally positively electrical, others negatively electrical; and if such bodies are presented to each other, their particles will be disposed to unite, and these different elec-

trical energies being present perhaps in different degrees, may give rise to different forces of attraction. The phenomena of galvanism undoubtedly establish the important influence of electrical energy on chemical affinity.

In the production of the different effects arising from the operation of galvanism, a different law is observed with regard to each, in relation to the structure of the galvanic apparatus. By increasing the number of plates in a battery, its power is enlarged, and, by having these plates of a large size, it is likewise obvious that the quantity of power generated must be greater. But the fact, rather singular, has been established, that an increase in the number of plates, without a proportional increase in their extent of surface, does not equally augment all the effects from galvanism, a different law being followed in the power of elevating temperature, of exciting sensations in the organs of animals, and of producing chemical decomposition.

This is apparent from a very simple fact. If a few large metallic plates, of a large surface, as 12 or 15 square inches, be employed as a galvanic battery, it will be powerful in producing light and heat, and will therefore illuminate charcoal vividly, or cause metallic leaves, placed in the circuit, to burn with great brilliancy. But it will display little power of electrical attraction and repulsion, and act feebly on imperfect conductors in producing decomposition. If the same plates be cut down, each being divided into four, and a battery be constructed with these, though there is, on the whole, the same quantity of surface, yet the relation of this to repetition or number being changed, the effects are different; it has little power in burn-

ing the metallic leaves; while it exhibits more evidently the different electrical states, it excites more forcibly sensations or contractions in animal organs, and is much more powerful in giving rise to chemical decomposition.

This has been in particular investigated by Ritter, and he, from a very extensive series of experiments, has endeavoured to establish the relation between number and surface in the metallic plates in a galvanic battery, adapted to the production of each of the effects obtained from galvanism. That of exciting sensations and contractions in animals, he found to be principally dependent on number; that of producing combustion is principally dependent on extent of surface; that of producing chemical decomposition is, in its relation to surface and number, intermediate between these. But with regard to all of them, a certain relation exists, or a certain proportion between number and surface gives the maximum, and, increasing either indefinitely, according to Ritter, diminishes the power. If the due proportion be observed, the galvanic energy displayed in all these effects may probably be indefinitely increased.

The theory of these differences probably is, that a peculiar state of intensity of galvanism is required for the production of each of these effects. The quantity of electricity generated in the apparatus will be proportional to the surface acted on, but its state of intensity is produced by its accumulation, and will therefore be regulated by the quantity of imperfect conducting compared with perfect conducting matter in the arrangement. The liquid interposed between the metallic plates is the least perfect conducting matter: the repetition, therefore, of the

metallic plates, the absolute surface remaining the same, forms an arrangement in which the imperfect conducting matter is most abundant, in which there is the greatest resistance to the evolution of the electric force, and in which therefore this will acquire the highest state of intensity. Now, a considerable intensity is requisite to enable the electricity to penetrate the animal membrane, which it must do to excite sensations or contractions, this membrane being an imperfect conductor: at a lower intensity, it will penetrate liquids, and act in decomposing them; and metals are conductors so perfect, that in the lowest state of intensity it will penetrate them, and produce effects proportional to its quantity. Hence the cause of the peculiar relations of number and surface to these different effects which have been proved to exist; the extent of surface giving quantity, and the repetition of surface in the series or number increasing the intensity.

In conformity to the difference of power thus required to produce these different effects, it has been found that different liquids are adapted to each. To excite that effect by which intense heat and light are excited, measured by the length of metallic wire which is melted, nitric acid, diluted with from 20 to 30 parts of water, is most powerful; sulphuric acid diluted is inferior in power, and the action of both in producing excitation is soon exhausted. For producing chemical decomposition, muriatic acid is better adapted, and it has the farther advantage of its power continuing longer; eight ounces may be added to a gallon of water, or a smaller quantity to a solution of sea-salt.

battery; and Davy, employing a similar arrangement, has even demonstrated that the principles of the decomposed substance are conveyed to a distance, and collected around the positive and negative wires, as they are by galvanism in its usual form.

On the hypothesis that electricity and galvanism are the same, it remains to be determined by what cause it is evolved, and put in motion in the galvanic arrangements. Two explanations have been given of this subject, one originally proposed by Volta, the other originating with the British chemists.

Volta's hypothesis rests on a fact, which he proves by experiment, that "if two different metals, perfectly dry, insulated, and having only their natural quantity of electricity, be brought into contact, on removing them from that contact, they are in different electrical states; the one is positive, the other negative." In the example of the metals now generally used in galvanic arrangements, the zinc is in the former state or *plus*, the copper in the latter or *minus*. The difference is not very considerable; it is perceptible, however, and, when accumulated in an electric condenser by repeated application of the plates, becomes sufficiently strong to cause the electrometer to diverge. Electricity, therefore, is developed by the mere contact of different metals, independent of any foreign action on them; or one metal, by its contact with another, forces part of its electricity into that other, and this inequality of distribution continues while they are in contact, and no conductor is applied to them. On this principle the action of

the usual galvanic arrangements is explained in the following manner.

If a series of metallic plates were constructed, without any intermediate substance, no accumulation of power would be obtained. The copper, for example, commencing this series, and in contact with a plate of zinc above it, would yield to it part of its electricity, and the zinc would become positively charged. But if another plate of copper were placed above the zinc, this action would be interrupted; the zinc being in contact at each of its surfaces with the two plates of copper, two equal forces would act in opposite directions, and destroy or counterbalance each other. The difference in the electrical state, therefore, of a series thus formed, would not be greater in the whole, than in a single pair of the plates, and would even amount to nothing if the arrangement began and ended with the same metal. But if a piece of moist card or cloth be placed between the plates, that is, between the zinc plate and the second copper plate, the effect of the latter on the former is interrupted: the liquid in the card having comparatively with the metal little of this peculiar electro-motive power, or property of breaking by contact the equilibrium of electricity, does not check the motion, but acting as a conductor, conveys the positive electricity from the zinc to the next copper plate; and accordingly, on this addition of the moistened card, Volta finds, by experiment, that signs of electricity are manifested. By continuing the series the power is always increasing, the action is renewed at each pair of plates, the electricity communicated is always given at the expence of the pieces beneath; these

therefore become negatively charged in a progressive order downwards; the others become positively charged in a similar order upwards: the two plates in the middle of the column are in the natural state; and as highly negative as the copper commencing the series is, as highly positive is the zinc plate which terminates it, the difference being greater according to the number of plates. The different powers of the different metals in affording galvanism, Volta ascribes to the different degrees in which they possess this electro-moving power, or to the effect of breaking the electric equilibrium, being greater in some than in others, zinc taking electricity from every other, and gold yielding it to the rest. The powers of different liquids in exciting galvanism, he supposes owing to their greater conducting power, modified as they have less of the electro-motive quality; and he shews by experiment, that saline liquors, which are superior to water in exciting galvanism, are superior in conducting power. The action which puts the electrical energy in motion, though greatest between the metals, is not peculiar to them; it exists, though to a less degree, in other substances, and hence a galvanic series can be constructed without metallic matter. And were we possessed of any solid substance capable of conducting electricity without having the electro-motive property, we might by means of it construct a galvanic battery without the intervention of any liquid.

The hypothesis opposed to this, considers the excitation of galvanism as the consequence, not of the action of the metals on each other, but of the chemical action of the liquids employed in the construction of the galvanic series

on the metals composing it. The following is the mode in which its evolution, and the determination of its motion are explained on this hypothesis. The commencing series is copper, zinc, and liquid either a saline solution or a diluted acid; a chemical action is exerted between this liquid, and the contiguous surface of zinc, and in consequence of it the electricity is evolved, or passes from the substance of the zinc to the surface acted on; the plate, therefore, becomes negative,—a state which is communicated to the copper on its opposite side. The electrical current is thus determined, or it passes from the zinc through the liquid; it is brought to the next plate: were this zinc, a chemical action would be exerted between it and the fluid, and a current in an opposite direction, by which each would be neutralized, would be formed; but being of copper, and the chemical action being always on the more oxidable metal, the copper merely conducts the electricity to the next plate of zinc; at the other surface of this zinc plate, a fresh portion of electricity is added to the current, by the chemical action which is there exerted; this is repeated at each of these plates; the quantity of electricity is increased as the current proceeds; and hence the last zinc plate of the battery must be in a positive state, while the other extremity is negative.

There is some difficulty in deciding on the merits of these hypotheses, though that of Volta is on the whole superior to the other. It has the important advantage of resting on a principle which is sufficiently established, that two metals by mere contact alter their electrical states. And, from this principle, combined wtth the fact, which

appears also to be proved, that the interposed liquids have little of this electro-motive power, while they are conductors of electricity, it appears to follow that from such an arrangement as that which constitutes the galvanic apparatus, a stream of electricity must be put in motion, and the two extremities of the series must be in the opposite electrical states.

The principal difficulty which attends it, and which affords some ground for the opposite hypothesis to rest on, is that the power of the interposed liquids, in exciting galvanism, does not appear to be proportional merely to their superior conducting power, but to be connected with the chemical action they exert; those being most powerful in exciting it which act chemically with greatest energy, and the excitation in a great measure ceasing when that action ceases. Yet this difficulty is perhaps counterbalanced by the opposite fact, equally established, that the power of certain liquids in exciting galvanism is more than proportional to their chemical action; alkaline solutions, for example, or solutions of sea-salt or sal-ammoniac, affording, next to diluted acids, the liquids best adapted to excite galvanic, though they do not exert any great chemical energy; and in comparing them with these acids, their exciting power is unquestionably much greater than their chemical action. If chemical changes, therefore, at all operate in the production of galvanic electricity, it is probably only as a subordinate cause, modifying the more important one from the electromotive power.

PART II.

OF THE CHEMICAL PROPERTIES AND COMBINATIONS OF INDIVIDUAL SUBSTANCES.

THE Science of Chemistry divides itself into two great departments,—the one including its general principles, or the statement of the phenomena and laws of those forces from the operation of which chemical changes arise; the other comprising what relates to the operation of these forces on individual substances, embracing therefore the history of the combinations of matter, and the chemical agencies of all known bodies.

I have given the outline of the methods, according to which substances may be classed, in conformity to their chemical relations. The table of the arrangement I have framed is prefixed to the first part of this volume, and it is unnecessary to repeat the observations with which it is accompanied. The first place is given to Atmospheric Air and its Elements, as there are no substances, the chemical actions of which are more important and extensive, and none therefore with which it is more necessary to be acquainted, in proceeding to the details of the science.

BOOK I.

OF ATMOSPHERIC AIR AND ITS ELEMENTS.

The atmosphere is that mass of elastic fluid which surrounds the globe. This aërial fluid was regarded as an element in the system of ancient philosophy; and one of the most brilliant discoveries of modern chemistry is that of its composition, first clearly demonstrated by Scheele. It consists of two aëriform bodies, oxygen gas, and nitrogen gas; with which are mixed, a small portion of another elastic fluid, carbonic acid, probably originating from accidental sources, and watery vapour in variable proportions derived obviously from the evaporation of water at the surface of the earth. The two latter substances are therefore scarcely regarded as essential to its constitution.

The composition of atmospheric air is demonstrated both by analysis and synthesis. The analysis is performed by submitting it to the action of substances which combine easily with oxygen, and reduce it from the aërial form, such as phosphorus, or the compound liquor formed by boiling sulphur with lime and water: a diminution of volume, amounting to about a fifth part, is produced, and the remaining air is wholly changed in its properties

being incapable of sustaining combustion or animal life. It is nitrogen gas; and the oxygen with which it was united is found to be combined with the substance by the action of which the change has been effected. The synthetic experiment consists merely in mixing oxygen and nitrogen gases in the due proportions, about 21 of the former with 79 of the latter by measure, when an elastic fluid is formed perfectly similar to atmospheric air. To be enabled to explain the chemical agencies of the compound, it is necessary, first, to describe the properties of its constituent parts.

CHAP. I.

OF OXYGEN GAS.

This elastic fluid was discovered nearly about the same time by Scheele, Priestley, and Lavoisier. It received the appellations of Fire Air, Dephlogisticated Air, Pure Air, and Vital Air,—terms superseded by the name of Oxygen, derived from a chemical property eminently characteristic of it, that of giving sourness or acidity to the compounds in which it predominates. Oxygen denotes its gravitating matter or base; Oxygen Gas is the name given to it in its elastic form.

This aëriform fluid is extensively diffused. It not only exists as a constituent principle of the atmosphere, but it

is also the principal component part of water; it exists in all acids, and is found in numerous forms of combination in mineral substances, and in the products of the vegetable and animal systems.

It is from some of its compounds that it is obtained insulated. That which affords it most readily is the mineral substance known by the name of Black Manganese. This consists of a peculiar metal, manganese, united with oxygen. If exposed to a full red heat, a large portion of the oxygen is expelled in the aërial form; the elevated temperature weakening the affinity between the metal and the oxygen, and allowing the latter to escape from the combination, until the increase thus produced in the relative quantity of the manganese to the oxygen that remains, adds so much to the force of its attraction, that the farther decomposition is prevented. The expulsion of the oxygen from the black oxide of manganese is much facilitated by the introduction of another affinity, so that if mixed with its own weight of sulphuric acid, a large quantity of oxygen gas is disengaged from the mixture by the heat of a lamp: the acid favouring its escape, by the attraction which it exerts to the manganese, in a low state of oxidation. Other metallic oxides, as the red oxide of mercury, or the red oxide of lead, afford a portion of oxygen by similar processes; a large quantity is obtained when nitre is decomposed by heat in an earthen retort: another salt, the oxymuriate of potash, affords it, when exposed to a red heat, and in a state more pure than that in which we obtain it by other methods.

Oxygen gas is colourless, and destitute of smell or taste;

it is rather heavier than atmospheric air; being about 1127, the latter being 1000.

This gas is absorbed by water, but in very sparing quantity; 100 cubic inches of water, freed from air by boiling, absorbing not more than 3.55 cubic inches, under a common atmospheric pressure, and at the temperature of 60°. By increasing pressure, a larger quantity is absorbed, proportional to the pressure applied; and, under a great pressure, water may be made to take up about half its bulk of the gas, acquiring, however, from this impregnation, no taste or smell.

The most characteristic property of oxygen gas is its power of exciting and supporting combustion. When an inflammable body is kindled and introduced into it, the combustion is rapid and vivid; the combustible body burns longer, and is more quickly consumed, and much more heat and light are evolved, than when it burns in atmospheric air; and even bodies which do not suffer combustion, when raised to a red heat in atmospheric air, as iron, burn rapidly when they are at this temperature immersed in oxygen gas. Strictly speaking, it is the only gas that supports combustion, atmospheric air and others doing so only from the oxygen they contain. During the burning, the oxygen is consumed, or is absorbed by the burning body; and hence a given quantity of it can support the process only for a limited time. The result of the combustion is frequently the production of a substance having acid properties; and from this, oxygen has been regarded as the principle of acidity.

Oxygen gas is also distinguished by its power of sup-

porting animal life. If an animal be confined in a given quantity of it, it lives a longer time than it would do in the same volume of atmospheric air. A quantity disappears, or is consumed during respiration, and is indispensable to the continuance of life; and atmospheric air, or any gas, sustains life, only from the oxygen it contains and is capable of affording to the blood. Pure oxygen, however, does not appear to be well adapted to animal existence. If an animal be confined in a given quantity of it, its respiration becomes hurried and laborious before the whole of the oxygen is consumed, and it dies even though so much oxygen is still present, that another animal of the same species, introduced into the residual air, will live. Hence the adaptation to animal life of an atmosphere such as ours is, in which oxygen is diluted with another air, which appears to be nearly negative in its effects.

Oxygen has a tendency to combination, more extensive perhaps than any other chemical agent has. It is necessary to support combustion, and during that process it combines with the combustible body. The products are compounds of oxygen, and are numerous and important agents in chemistry. The acids are of this kind, and their activity is principally dependent on their oxygen, which they yield readily to other bodies, and which, by the dense state in which it exists, is often capable of exerting powerful affinities. All the metals are capable of combining with this principle. And it exists in an immense number of natural substances. It is unquestionably more abundant in nature, and more extensively dif-

fused than any simple body: its affinities are more numerous and more energetic; the development of its agencies formed the principal part of what has been named the modern theory of chemistry, and still affords the most important relations of the science.

CHAP. II.

OF NITROGEN GAS.

This elastic fluid remains after the removal of oxygen from atmospheric air, by the processes which have been described. It is most easily procured by burning phosphorus in atmospheric air, or exposing this air to the liquor, formed by boiling sulphur and lime with water: in either case the oxygen gas is abstracted, and the residual nitrogen gas is agitated with water to render it pure. Nitrogen is also disengaged from animal substances, acted on by diluted nitric acid. It has been known by various appellations, as Corrupted Air, Mephitic Air, Phlogisticated Air. It received the name of Azote or Azotic Gas, from being, in opposition to oxygen, incapable of sustaining animal life by respiration. The more correct denomination of Nitrogen is given to it, from being the base of an order of compounds which have been long known by the name of Nitrous.

Nitrogen gas is permanently elastic, invisible, insipid, and inodorous. It is lighter than atmospheric air; its specific gravity being to that of the latter as 966 to 1000.

This gas, possessing no very striking property, is principally characterized by certain negative qualities in its pure form, and by the nature of the compounds it forms. Thus it is incapable of supporting combustion. It is equally incapable of supporting animal life by respiration. It is not inflammable; for although it combines with oxygen, a process generally attended with the phenomena of combustion, nitrogen presents the anomaly of exhibiting none of the appearances of burning during this combination; it neither sensibly evolves heat nor light. Lastly, nitrogen gas is not perceptibly absorbed by water; it suffers no apparent diminution of volume when exposed to it. If, however, the water has been previously freed from all air by boiling, and the nitrogen gas be exposed to it for some hours, a very small quantity, 1.47 cubic inch, is absorbed by 100 cubic inches of the water.

Nitrogen exhibits more distinctive characters in the combinations into which it enters. It unites with oxygen in different proportions, and forms compounds possessed of very peculiar chemical properties. It unites too with hydrogen. And it is a chief ingredient in the products of the animal system, and appears to give their most distinguishing chemical characters.

Opinions have often varied with regard to the nature of nitrogen, and certain facts were observed which rendered the investigation of this difficult. Priestley stated many

experiments in which nitrogen gas appeared to be procured from water by peculiar processes. Thus, in distilling water from an earthen retort, or in passing it through an earthen tube at a red heat, an elastic fluid was always obtained, consisting chiefly of nitrogen. In the freezing of water, a portion of elastic fluid is disengaged, which Priestley found also to be nitrogen; and the production of this appeared to him to be unlimited. A given portion of water, which had been previously freed as much as possible from any air it might hold dissolved, being made to freeze in a tube, gave out air; and when this was removed, and the water melted without exposing it to the atmosphere, still, on freezing it, there was the disengagement of nitrogen gas. Girtanner gave an extensive series of experiments, affording similar results with regard to the production of nitrogen in converting water into vapour. He concluded from them, that nitrogen is, like water, a compound of oxygen and hydrogen, containing a smaller proportion of oxygen than water does; atmospheric air, therefore, he supposed to be a compound of oxygen and hydrogen; and the nitrogen gas obtained from it by the usual methods he supposed to be formed by a portion of the oxygen being abstracted, and the remaining quantity entering into combination with the hydrogen. Priestley had drawn different conclusions. Water he regarded as probably a simple body, and the basis of all elastic fluids, appearing under the form of nitrogen, hydrogen and others, by modifications produced on it by the operation of more subtle principles which we are not able to ascertain by weight.

These hypotheses were generally regarded as extravagant, and nitrogen gas was in the system of Modern Chemistry held to be a simple substance. The late discoveries, however, by the application of galvanism, have appeared to establish facts with regard to it which preclude this supposition. Ammonia is a compound of nitrogen with another elastic fluid, hydrogen; and when this compound is submitted to the action of potassium, the base of potash, aided by heat, an olive-coloured substance is obtained, the ammonia disappears, and a portion of hydrogen is evolved. The solid substance, Mr Davy inferred, from its formation, and from the results of its analysis, is a compound of the potassium with the nitrogen of the ammonia, and a little oxygen derived, either from moisture, or perhaps existing as an element of ammonia. When decomposed by heat, it gives out nitrogen with a portion of hydrogen, and a little ammonia; but the most singular fact is, that in this decomposition less nitrogen is obtained than what ought to be given out. Since, therefore, nitrogen is not evolved in the first experiment, when the ammonia is decomposed by the action of potassium, and since the quantity of it given out in the decomposition of the substance formed by that action, is not equal to what ought to be evolved from the quantity known to exist in the composition of ammonia, there is an evident loss of it; and this loss of nitrogen, Mr Davy farther finds, is accompanied with a production both of oxygen and nitrogen.

From these singular results, if no source of fallacy can be supposed present, it follows, that nitrogen has some peculiar relation both to hydrogen and oxygen. The most

obvious suppositions are, that it may be an oxide of hydrogen; or that both it and hydrogen may be compounds of one elementary matter, the base of ammonia. But we have no facts from which the question can be decided; Mr Davy's subsequent investigations have indeed rather thrown doubt on the former conclusions, as they point out some circumstances whence the loss of nitrogen and production of hydrogen might be in part accounted for, without supposing the nitrogen to be decomposed. Yet even these are not so unequivocal as to be altogether decisive, and the opposite view, as Mr Davy remarks, may still be defended.

The idea of the composition of nitrogen derives no support from the original observations from which it was inferred, the production of it in passing water through ignited earthen tubes, or in the freezing of water; for, with regard to the former, it has been shewn to arise from the admission of atmospheric air from the porosity of the tube; and, with regard to the latter, Mr Davy has found, that when care is taken to exclude the admission of atmospheric air, the production of aërial matter is very limited, and what does appear is probably atmospheric air, and merely the small portion of it held by water in a state of solution. The nature of nitrogen, therefore, remains at present wholly in obscurity.

CHAP. III.

OF ATMOSPHERIC AIR.

For the discovery of the composition of atmospheric air, chemistry is indebted to Scheele. The following is the experiment from which he inferred it: Having put into a bottle, capable of containing 24 ounce measures, four ounces of a liquor prepared by boiling a solution of potash on sulphur, and having closed the bottle accurately, and inverted it in water, he allowed it to remain in this situation for two weeks. At the end of that time, he opened the bottle under water, when a portion of water immediately rushed in, shewing that part of the air included with the liquor had been absorbed, or lost its elastic form: the quantity which had disappeared amounted to six parts nearly of the original twenty. The remaining air was changed in its qualities, was lighter than atmospheric air, and incapable of supporting combustion.

Scheele had previously discovered the existence and properties of oxygen gas, and by this discovery he was enabled to explain the nature of the changes which the atmospheric air had undergone. Since it was diminished in volume, it was obvious that a portion of elastic fluid had been abstracted from it; and since it was also changed in its qualities, and in particular was no longer capable of supporting combustion, it might be inferred, that it had

not been a portion of the entire air that had been absorbed, but a principle which gave it that property. Scheele accordingly concluded, that oxygen gas had been abstracted from it, the entire air being a compound of this with the residual gas, which is nitrogen. He found, what was conformable to this, that oxygen gas is absorbed by the solution of sulphur and potash by which the diminution in the volume of atmospheric air had been produced. And he farther confirmed his conclusions synthetically, by adding oxygen gas to the residual nitrogen when an air similar to atmospheric air was produced. He found, that similar changes are produced in atmospheric air by other substances which are capable of abstracting its oxygen.

Lavoisier soon after advanced the same opinion with regard to the composition of atmospheric air, from experiments in which its oxygen was abstracted by burning inflammable bodies or calcining metals in it. From some of the compounds formed in these processes, particularly in the calcination of quicksilver, he obtained the oxygen which had disappeared, and adding it to the residual nitrogen gas, reproduced atmospheric air. The composition of this air, therefore, is demonstrated, both by analysis and synthesis.

The process by which the proportion of oxygen in atmospheric air is determined, has been named Eudiometry, from an opinion which at one time was entertained, that the salubrious power of the air with regard to animal life depends on oxygen, and that therefore by this process we might be able to ascertain this,—an opinion for which there is no foundation. Different eudiometrical methods

are employed, such as the action of the liquor prepared from sulphur and potash, or sulphur and lime boiled in water, the slow combustion of phosphorus, the detonation of the air with hydrogen gas, and the action of nitric oxide gas,—applications to be noticed under the history of these substances.

The proportions of oxygen and nitrogen in the atmosphere have been variously estimated, from the diversities arising from different eudiometrical processes. The average result from those experiments that can be regarded as most accurate, is 21.5 of oxygen gas to 78.5 of nitrogen gas by measure, or 22.5 to 77.5 by weight.

It has been supposed, that the composition of atmospheric air varies at different parts of the earth's surface, and also at different heights. The reverse of this, however, has been sufficiently established, and, by more recent experiments, made with every precaution, it has been shewn, that air, in the upper regions of the atmosphere, is the same in composition with air at the level of the sea, and that there is an equal uniformity in composition in the air of distant countries. It is also uniform, according to De Marti's experiments, in every state of the atmosphere with regard to temperature, pressure, humidity, the season of the year, or the hour of the day or night. What appears rather more singular, the same experiments prove what Priestley had indeed before established, that the air of places the most offensive and unhealthy, is of the same sensible chemical composition as that of situations the most salubrious; the air of crowded cities, or of manufactories, being not less pure than that of the coun-

try; the deleterious agency, therefore, of such air, depending not on any difference in composition, but on the presence probably of more subtle effluvia, unfavourable to health.

In the composition of atmospheric air, there is a striking singularity, which requires to be pointed out. Its constituent gases are of different specific gravities, and therefore, were they not retained in union by a mutual attraction, it might be concluded that they must separate; the heavier, that is, the oxygen, collecting towards the surface of the earth, the lighter receding from it, and occupying the upper region,—a separation which, it appears from the preceding facts, does not take place. Yet, although they remain united, there are none of the usual indications of chemical union, no modification of properties, and even no change of density. What, then, is the nature of that constitution by which they are preserved in a state of equal and uniform diffusion?

To solve this problem, a very ingenious hypothesis has been advanced by Mr Dalton, founded on the assumption, that the particles of mixed gases neither attract nor repel, but are perfectly indifferent with regard to each other. Did they attract, Mr Dalton conceives, they must enter into intimate combination, which would be marked by a change of properties. Did they repel each other, they must separate, and be arranged according to their specific gravities. Either supposition, therefore, he concludes, is excluded by the known constitution of the atmosphere; and there remains only the hypothesis, that the particles of the elastic fluids composing it neither attract nor repel,

nor are indeed at all affected by their proximity. On this hypothesis, each gas diffuses itself from the repulsion between its own particles, and there rest, upon the surface of the earth, so many columns, as it were, of these gases, each supporting itself by its own elasticity, intimately blended with the others, but altogether independent of each other. And as the diffusion is complete, we discover, in any given portion of the mass, these gases in the same relative proportion.

Another hypothesis may be proposed on this subject, resting perhaps on a principle more probable *à priori*, and equally adapted to explain the constitution of atmospheric air. The most correct views of chemical affinity lead to the principle, that all bodies have mutual attractions, and that these are prevented from operating, so as to establish intimate combination only by the exertion of external forces. In the action of a liquid on a solid, cohesion operates, counteracting the mutual attraction, and, if sufficiently powerful, preventing solution. In the action of an aërial substance on a solid, the cohesion of the one, and the elasticity of the other, are the obstacles to the effective exertion of the attraction exerted between them. And in the case of two aëriform fluids presented to each other, the same elasticity in each is the cause counteracting that affinity which would unite their particles. But in all these cases, it is not to be supposed that the affinity is not exerted: it no doubt operates with a certain force, the circumstances which act against it only being so powerful as to prevent intimate combination. The particles of oxygen and nitrogen gases are capable, under

certain circumstances, of exerting a strong attraction, and entering into intimate combination. Under the circumstances in which they are presented to each other in the atmosphere, this attraction is not exerted so as to overcome the elasticity of each, and establish this combination. But still it exists, and may so far operate as to counteract the slight difference in their specific gravity, and retain them in slight union. This accounts satisfactorily for the phenomena, and, in particular, reconciles the two facts, which appear incompatible, the uniformity of the composition of atmospheric air, while it has no properties different from those of its constituent parts. The principle, too, in the abstract, is more probable than that of the opposite hypothesis. The particles of any individual gas repel each other: why therefore should the particles of mixed gases not exert a similar repulsion? It is scarcely possible to conceive any cause for this, but the exertion of a mutual attraction not sufficiently powerful to overcome their elasticity, and bring them into intimate combination, but exerted at least with such force, as to counteract their repulsion, so as to prevent their separation.

Besides the oxygen and nitrogen which principally compose the air of the atmosphere, there always exists in it a sensible quantity of a compound elastic fluid, Carbonic Acid Gas. This is easily discovered, by exposing to the atmosphere, substances which have an attraction to this gas, as lime water, or an alkaline solution; they are soon found to have imbibed a portion of it. The proportion of this gas to the other gases composing the atmosphere is so small, that it is not easy to estimate it with

accuracy. It has been supposed to amount to a hundredth part. Mr Dalton has inferred, from experiment, that it does not exceed a thousandth by weight. As this gas is produced in respiration, and in other processes at the surface of the earth, the portion of it contained in the atmosphere has been supposed to be derived from these sources. This is not improbable; at the same time, from the reciprocal attraction which gases exert, it is uniformly diffused; and it appears also to be present always in nearly the same proportion, and at the greatest heights at which the air has been examined.

Aqueous vapour is another constituent part of the atmosphere; in quantity, however, very variable, and obviously derived from the evaporation of water at the surface,—an operation dependent on temperature and other causes, and therefore not uniform. The temperature is the great cause by which the quantity is varied, and hence the proportion of watery vapour in the atmosphere is much dependent on climate and season. In the torrid zone, Mr Dalton remarks, its quantity is such as to exert a pressure on the surface of the earth equal to from 0.6 to an inch of mercury: in our climate it is seldom equal to a pressure of 0.6, and in winter is sometimes so low as 0.1. While it preserves completely the elastic form, the air through which it is diffused is perfectly transparent. When condensing, it communicates a degree of opacity, and, according to the extent and rapidity of the condensation, gives rise to the appearances of clouds, dew, mist, and rain.

A subject of chemical inquiry is, by what operation is water elevated in vapour in the atmosphere? and, what is strictly connected with this, in what state does the aqueous vapour exist? Water, being capable of passing into vapour from the action of heat alone, it has been supposed that its elevation in the atmosphere is entirely the result of temperature; the vapour formed existing, according to one view, in a state merely of mechanical diffusion, or independent of any action of the permanent gases upon it, or, according to a different hypothesis, being combined with these gases by a weak attraction. According to a different theory, the transition into vapour is owing to the chemical affinity exerted to water by atmospheric air, and of course it is retained by that air in a state of solution or weak combination.

This last theory, proposed by Halley, and afterwards illustrated by Le Roy, Hamilton and Franklin, is probably the just one. A mutual affinity exists between water and the gases composing the atmosphere, for it absorbs them in sensible quantity; the same affinity must operate in enabling these gases to dissolve a portion of water, and this is promoted, like all similar combinations, by a high temperature, by agitation, and of course also by the dryness of the atmosphere. The opposite views rest on an assumption extremely doubtful, that water, independent of any chemical action of the air upon it, can pass into vapour at natural temperatures. The proof which has been usually given of this is, that water, placed *in vacuo*, passes into vapour at such temperatures. But the proof, from the manner in which the experiment has been performed,

is altogether inconclusive. A little water is placed in the jar of the air-pump, and the air is exhausted, or it is introduced into the barometer, and of course into the more perfect Torricellian vacuum. But in either case the pressure of the atmosphere is withdrawn, along with its chemical agency; and although a portion of water may, under these circumstances, pass into vapour, this is no proof that the same thing will happen under the usual atmospheric pressure. The experiment to be conclusive must be performed under a pressure equivalent to that of the atmosphere, that is, equal to a column of mercury 29½ inches in height. But the result is then subversive of the hypothesis; for water, under that pressure *in vacuo*, does not sensibly evaporate.

It is probable, therefore, that the spontaneous evaporation of water, exposed to the atmosphere, depends principally on the attraction exerted to it by the elastic fluids which form atmospheric air, and the aqueous vapour existing in it may be regarded as in the same state of slight union with the other gases composing it, as they are with each other. The only difference is, that they, being so far distant from the point at which they assume the aëriform state, are not affected by natural changes of temperature, while these changes must effect the combination so far as it relates to the aqueous vapour.

Another chemical question of considerable interest, but still involved in difficulty, relates to the causes by which water is precipitated from the atmosphere, or the theory of rain. It is obvious, that it may be occasioned by reduction of temperature, but it is not easy always to trace this

cause, and especially to account for the deposition being so sudden and copious. Hutton advanced the hypothesis, that the solvent power of air, with regard to water, is increased by temperature in a higher ratio than the increase of temperature itself; and hence, if two portions of air, at different temperatures, are mingled, as they may be in the atmosphere by winds, the whole quantity, if each has been previously saturated with humidity, will be incapable of retaining in solution all the water which the separate portions held dissolved: a quantity therefore will be rapidly separated, and its particles, uniting and meeting with resistance in their descent, will coalesce so as to form rain. The principle of this hypothesis, however, is not established, and it is even perhaps more probable, *à priori*, from theory, that the solvent power should proceed in a decreasing ratio with regard to temperature, the increase of temperature augmenting the elasticity, which is an obstacle to the combination. Electricity has sometimes been supposed to be concerned both in the spontaneous evaporation of water, and in its deposition from the atmosphere, but the facts with regard to this are not well ascertained.

The atmosphere, then, so far as its constituent parts can be ascertained by chemical analysis, consists of oxygen, nitrogen, carbonic acid, and aqueous vapour; the three first are in constant, the last in variable proportions; but taking the mean, the following may be given as the relative quantities of these principles:

Nitrogen gas,	77.5	by measure,	75.55	by weight.
Oxygen gas,	21.	———	23.32	———
Aqueous vapour,	1.42	———	1.03	———
Carbonic acid gas,	.08	———	.10	———

The properties of atmospheric air are simply those of its constituent gases, weakened by their mutual dilution. It is invisible, insipid, inodorous, compressible and permanently elastic. Its specific gravity is .0012279,—the medium, as nearly as can be estimated, between the specific gravities of oxygen and nitrogen gases, in the proportions in which they are mixed in the atmosphere.

Atmospheric air supports combustion, a power dependent on its oxygen. From the operation of the same principle, it sustains animal life in respiration. The action of the nitrogen is negative in both processes; it serves therefore merely to weaken the action of the oxygen.

Water absorbs atmospheric air, though in sparing quantity. The absorption, too, appears to be unequal with regard to its constituent parts, more of the oxygen being absorbed than of the nitrogen. By agitation of a small portion of air with a large quantity of water, the whole of its oxygen may even be abstracted, while the greater part of the nitrogen remains unabsorbed. Hence all water exposed to the atmosphere holds air, chiefly oxygen, dissolved, and it is difficult to expel this air from it entirely.

Atmospheric air is, from its chemical powers, an important agent in many chemical and natural processes. It equalizes temperature over the globe, and distributes water. It sustains life in respiration, and is necessary in the process of vegetation. And by its chemical action it slowly effects changes in the greater number of substances which are exposed to it.

An interesting subject, but one extremely obscure, re-

lates to the natural processes by which the purity and uniform composition of the atmosphere are preserved. By respiration, and many other chemical changes going on at the surface of the earth, there is a constant consumption of its oxygen, and, by many of these processes, there is also a production of carbonic acid gas, by both of which the composition of the air must be altered, and its purity considered in relation to animal life impaired. Yet we do not find that any sensible deterioration takes place; and indeed we have proof, from its adaptation to the processes of nature, that its composition must have always been the same. By what causes, then, is this uniformity of composition preserved? At one time it was imagined, that the vegetable kingdom performed this important function; growing plants absorbing, it was supposed, carbonic acid gas by their leaves, and exhaling oxygen gas. The two tribes of animated beings thus stood opposed to each other in their relations to the atmosphere, and presented an admirable view of adjustment in the economy of nature. There is, however, much reason to doubt of the facts on which this opinion rests, and, from more recent investigations, it appears even, that except when under the direct action of the rays of the sun, vegetables, like animals, consume oxygen, and form carbonic acid. There must therefore be other processes by which the changes in the atmosphere are regulated, and its purity restored;—processes probably depending on the relations which exist between oxygen, hydrogen, and nitrogen, and which the progress of the science may soon unfold.

CHAP. IV.

OF THE CHEMICAL AGENCY OF OXYGEN IN ITS PURE FORM, AND AS IT EXISTS IN ATMOSPHERIC AIR, AND OF ITS GENERAL CHEMICAL RELATIONS.

THE attractive power of oxygen towards other bodies is more extensive than that of any other chemical agent, and the history of its combinations forms perhaps the most important part of chemical science,—an importance which the progress of discovery is only more fully unfolding. The agencies of this element admit of some general observations; and as they are exerted by it both in its pure form, and as it exists in atmospheric air, I consider these observations as best placed after the history of the atmosphere. They form the subject of the present chapter.

The most general phenomenon attending the combinations of oxygen, is the evolution of heat and light. This constitutes the operation of Combustion or Burning, the theory of which is first to be explained.

The phenomena of combustion, and the distinction of bodies into combustible or inflammable, and incombustible or uninflammable, are sufficiently familiar. The latter, when exposed to heat, have their temperature raised proportional

to the degree of heat applied; but when this is withdrawn, the temperature falls, and they return to their former state. Combustible bodies, on the contrary, when sufficiently heated, begin of themselves to emit heat: this is also accompanied with an evolution of light; and while these changes proceed, the body appears to be consumed, or at least it is converted into matter, which is no longer inflammable. It is this emission of heat and light, and apparent waste of substance, or change of properties, which constitute the process of Combustion.

Becher first endeavoured to explain these phenomena on chemical principles. Fire he considered as the effect of a peculiar principle, what he named Inflammable Earth, in a state of motion: this principle he supposed to exist in inflammable bodies, and when brought into this state, to exhibit the phenomena of burning. Stahl, without adopting the whole of this hypothesis, supposed that inflammables contain a common principle, the matter of heat and light, on which their inflammability depends; that the disengagement of this gives rise to the sensible phenomena of combustion, and that to its evolution the loss of inflammability is owing. He farther established, in conformity to these views, an important fact, that inflammability may be restored to the uninflammable product, by heating it with another inflammable substance,—a change which he ascribed to the transfer of the inflammable principle, or phlogiston, as he named it, from the one to the other.

This hypothesis appearing to afford a satisfactory explanation of the phenomena, was soon universally received, and, for a considerable period, no doubt was enter-

tained of its truth. In framing it, however, Stahl had not attended to the influence of the air in combustion; which, even before his time, had been demonstrated, and the nature of it in some degree ascertained, by the experiments of Mayow and Boyle. It was therefore defective in not accounting for the necessity of the presence of the air to the support of that process. It had farther been ascertained, that some bodies, instead of losing, gain weight in burning,—a fact inexplicable on the supposition that combustion consists merely in the disengagement of a principle from the burning body.

Various attempts were made to solve these difficulties, but with little success; and the discoveries which were soon after made of the chemical agencies of the elastic fluids, proved still more clearly the deficiency of the original doctrine. It was observed, that combustion proceeds more rapidly in oxygen gas than in atmospheric air; and it was farther shewn, that when it is carried on in atmospheric air, the volume and weight of the air are diminished, and the residual air is incapable of supporting that process,—changes which were farther proved to be owing to the consumption of oxygen. These facts led to different views. While the greater number of chemists laboured to reconcile them with the system of Stahl, two French chemists, Bayen and Lavoisier, considered them as leading to the subversion of the hypothesis. Bayen had observed, that from the calces of metals, as they were named, a large quantity of elastic fluid is given out on exposing them to heat with charcoal, or even with regard to some of them to heat alone, the metal being at the same

time reduced to the metallic form; whence he concluded, that the metal owes its calcined state, not, as the system of Stahl supposed, to the loss of phlogiston, but to its combination with this air. Lavoisier had at the same period traced still farther the agency of the air in combustion. He demonstrated, what in part indeed had been shewn by former chemists, though it had never been much attended to, that its volume is diminished during this process, the diminution ceasing when it proceeds to a certain extent; that the substance in burning increases in weight, and that from the product of the combustion, an elastic fluid may be obtained. The views suggested to him by these experiments, he gradually extended and strengthened by new researches. He at length established the simple principle, that combustion is merely the combination of oxygen with combustible bodies. And availing himself of the discovery of Black, of the large quantity of latent caloric peculiar to the aëriform state, he farther inferred, that the heat produced in burning is not derived from the combustible matter, but from the oxygen gas. With these conclusions were combined others, forming a system, in which the chemical relations of oxygen were developed.

The theory of Lavoisier rests on the following general facts: 1*st*, The presence of oxygen is indispensable to combustion: a combustible body being incapable of being kindled *in vacuo*, or in any air which cannot afford to it oxygen; or, if kindled, it is immediately extinguished in any of these situations: if, on the contrary, it be placed in pure oxygen gas, its combustion is more vivid than in atmospheric air. 2*dly*, The oxygen present is always con-

sumed, as is proved by the diminution of volume and abstraction of oxygen which attend combustion in atmospheric air: hence, too, a burning body, when confined in a certain quantity of air, burns only for a limited time, that is, until the oxygen present is consumed; while, in the same quantity of oxygen gas, it continues to burn much longer; the diminution of volume too is in this case greater; and were the oxygen gas pure, the whole of it might be spent in the combustion. *3dly*, In every case of combustion the combustible body increases in weight, an increase equal to the weight of the oxygen which disappears: this increase of weight indeed is not always apparent; on the contrary, it often appears that the weight is much diminished, or even that the body is entirely consumed; but this is owing to the product being one existing in the aëriform state, and therefore not evident to the senses: if obtained, however, and weighed, it is found to exceed the weight of the combustible body; and in every case of this kind, as well as where the product is a concrete substance, and of course more easily weighed with accuracy, the increase of weight is found exactly equal to the weight of the oxygen gas, which, during the combustion, had combined with the combustible body. *Lastly*, the oxygen which has disappeared during the process of combustion, can always be recovered from the substance formed by the process: it cannot always indeed be obtained in a pure form, for the affinity by which it is retained combined with the combustible body, is in general too powerful to be overcome by the mere application of heat; but it can always be procured by exposing the substance formed by the combustion to the action of another inflammable body, having a

stronger attraction to oxygen; the oxygen is tranferred from the former to the latter, and the substance which we know to be formed from that substance combined with oxygen is obtained; the quantity of this new product indicating the quantity of oxygen transferred, and this always corresponding with the quantity which had originally been consumed in the combustion. All these facts have been ascertained by experiments of great accuracy, and they establish the conclusion, that combustion consists in the combination of oxygen with combustible bodies: These bodies are substances having an attraction to oxygen: And the products of combustion are compounds of them with this principle.

This combination, like other cases of chemical action, is influenced by temperature: in general, heat requires to be applied to cause it to commence, the evolution of caloric from the combination itself being then sufficient to enable it to proceed. The heat operates by diminishing the cohesion of the combustible body which opposes the combination, and the degree of it will be regulated by the force of that cohesion, and the strength of the affinity between the oxygen and the combustible matter.

From the principle thus established, it remains to explain the phenomena which attend combustion,—the evolution of caloric, and of light.

With regard to the origin of the heat in burning, the popular notion appears at first view incontrovertible,—that it is derived from the burning body. It is more or less hot; no other agent appears to be concerned; and it appears nearly a self-evident conclusion, that the body, the

temperature of which is thus elevated, is the source of the caloric by which the elevation is produced. It is accordingly the conclusion which was received in the earlier hypotheses of Becher and Stahl.

The discovery of the influence of the air in combustion, at once invalidates the apparent strictness of the reasoning whence this conclusion was drawn; for, when it is discovered that combustion is not merely an affection of the combustible body, but is the result of its combination with a portion of the air around, it is obvious, that the heat may, with as much probability, *à priori*, be supposed to be derived from the one as from the other. Whether it proceed from the combustible matter, or from the oxygen gas, it must be evolved at the surface where the combination proceeds, that is, at the surface of the burning body: it is apparent to the senses, while the gas being invisible escapes observation; but still the caloric given out by the gas, and communicated to the substance in the act of combustion, may be the cause of its elevation of temperature.

When it was farther ascertained, as was done by the discovery of Black, that aëriform substances contain a large quantity of caloric peculiar to their aëriform state, it became even the more probable opinion, that the caloric evolved in combustion is derived from the oxygen gas, which in that process generally passes into a more dense, and often indeed into a concrete form. This accordingly appears to have been the first modification of this opinion that was proposed, the heat produced being supposed to be the latent caloric peculiar to the oxygen in its aërial form.

Another view of the subject, or perhaps rather a different mode of expressing it, was likewise proposed by Lavoisier. He regarded caloric as existing in bodies, and especially in those in the aëriform state, in a state of chemical combination, and supposed it to be disengaged in combustion from the oxygen gas, in consequence of the superior affinity of the combustible body to oxygen.

Crawford gave the explanation under a form less hypothetical, and more directly inferred from experiment. The general fact had been demonstrated, that different bodies at the same temperature contain different quantities of caloric,—a fact expressed by saying, that they have different capacities for heat. Irvine had farther shewn, that the capacity for heat is often changed by chemical combination. It occurred to Crawford, that this might happen during combustion, and, if it did, might give rise to the evolution of heat which attends the process; for, if the capacity be diminished, in other words if the capacity of the compound resulting from any combination be less than the mean of the capacities of its constituent parts, a portion of caloric must be rendered sensible, or produce an elevation of temperature. This led to an extensive experimental investigation, whence were established the general facts, that the capacity of oxygen gas for caloric is uncommonly great, that the capacities of combustible bodies are comparatively small, and that the capacities of the substances formed by combustion, though superior to those of combustible bodies themselves, are inferior to the mean of these and of oxygen gas. Hence an elevation of temperature must attend the combination, and the caloric

producing this must be derived from the oxygen gas, not from the combustible matter. In different bodies, the difference in the proportion between the capacities before and after combustion are different, and hence the quantities of caloric evolved are extremely various.

It is not difficult to determine which of these explanations is to be preferred. Crawford's involves no hypothesis; and if the experiments by which the capacities are determined be correct, or even be approximations to accuracy, it is simply what every philosophical theory ought to be, the expression of general facts. Nor is there any reason to call in question the general accuracy of the experiments, though, from the difficulty of the investigation, they may be involved in some errors, affecting not the principle, but merely the estimation of the quantities of caloric evolved.

The origin of the light in combustion is of more difficult explanation; at least we can have still less certainty of the justness of any opinion with regard to it. Lavoisier had supposed it to be derived from the oxygen gas, but without any conclusive evidence; for it is obvious, that the admission of the fact, that the caloric is evolved from this gas, is no proof that the light has the same source; at least without the assumption sufficiently improbable, that these two principles are the same.

We have perhaps no very decisive evidence, that the light is derived from the combustible body; still there are some facts which appear to render this rather the more probable opinion. Thus, light is often evolved, when

oxygen is transferred from one inflammable to another, and as the oxygen in its first combination has parted with its light, if it contained any, the light evolved in the second combination must be supposed to be derived from the inflammable body. Another fact, still more conclusive, is, that an evolution of light attends the combination of inflammable substances with each other, of which we have a striking example in the combination of sulphur with metals. This proves that light is a principle existing in these bodies, and as we have no similar proof of its existence in oxygen gas, it follows as the more probable conclusion, that the light evolved in the combustion of these substances is that which they are thus proved to contain. At the same time, it is to be remarked, that with regard to principles so subtle, our conclusions must in the present state of chemistry be somewhat uncertain; and the production of intense light by galvanism, without our being able distinctly to assign its origin, proves sufficiently that we are imperfectly acquainted with the chemical relations of this power.

Very different quantities of light are given out by different combustible bodies in burning; in general, the illumination is greatest from those which are in the state of vapour while burning; at the same time, this is not strictly necessary, some substances which remain fixed, as phosphorus or iron, giving very intense light. The constitution of the light emitted with regard to the different coloured rays, is also different in different bodies, some in burning giving white, others differently coloured light. This appears to be very much connected with the tem-

perature which accompanies the combustion. Those which burn with a low heat, as sulphur or ardent spirit, in general emit the blue or purple rays most copiously; those which burning produce a greater elevation of temperature, as charcoal, give the red rays; and where the temperature is high, and the combustion rapid, all the rays are emitted so as to constitute white light.

Besides the simple case of the combination of oxygen in the elastic form with bodies, which constitutes combustion, there are others rather more complicated, in which, after having been combined with one body, it is transferred from it to another.

Of this, the operation of Deflagration is an example. When an inflammable substance is mixed with nitre, on kindling the mixture, a very rapid combustion, attended with the disengagement of much heat and light, takes place, and this altogether independent of any action of the air. The theory of the operation is, that in nitre there exists a large quantity of oxygen in a concrete form, this salt consisting of nitric acid and potash, and this acid being composed of oxygen and nitrogen. These are not retained in union by a strong attraction; hence, when exposed to heat they separate, and, in deflagration, the oxygen being presented to the inflammable substance, combines with it rapidly, and causes it to burn. The nitrogen gas assumes the elastic form, mixed frequently with an aëriform product from the combustion. There is some difficulty in accounting for the high temperature produced by deflagration. Oxygen existing in the elastic form has a large capacity for caloric, and suffering a di-

minution of capacity in the combinations into which it enters, the temperature must be elevated. But existing in nitre in a concrete state, it is not to be presumed that its capacity will be equally great. In passing therefore into a new state of combination, there cannot be a diminution of capacity to the same extent, and hence there must be less caloric evolved. In some cases even of deflagration, the compound which the oxygen forms with the combustible body exists in the aëriform state, and reasoning from analogy, it must require more caloric to produce in it a given temperature than the nitre itself.

This difficulty perhaps cannot be entirely removed. It may be remarked, however, what so far lessens it, that the consumption of a given quantity of oxygen by deflagration, renders less caloric sensible than the consumption of the same quantity by combustion: thus, Lavoisier ascertained, that in the deflagration of charcoal with nitre, the heat evolved melted 29½ libs of ice, 1 lib. of oxygen being consumed; while in the consumption of the same quantity of oxygen in the common combustion of charcoal, the quantity evolved melted 37½ libs. It is also to be observed, that when oxygen combines with nitrogen, to form nitric acid, little caloric is set free; and again, when this acid combines with potash to form nitre, there is little disengagement of heat. We thus trace the large quantity of caloric in oxygen gas along with it into the solid salt, and hence may expect it to be evolved, when the oxygen is transferred to an inflammable substance. The only difficulty is, whether the large quantity of caloric, which would thus appear to be contained in ni-

tre, can be proved to exist in it from its known capacity, which according to this view ought to be great; and with regard to this, we have as yet no experiments that can be considered as decisive.

The origin of the light in deflagration, must be the same as that in combustion.

From the sudden and rapid extrication of aëriform matter, which attends deflagration, a high elastic power is exerted, especially as the elasticity of this is so much increased by the high temperature. This elastic power is of course greatest when, with the gaseous matter, from the decomposition of the acid of the nitre, there is an aëriform product from the combination of the oxygen with the inflammable. This happens in the deflagration of charcoal and of sulphur, and to this the expansive power of gun-powder, which consists of these ingredients with nitre, is owing. In some cases, the quantity of elastic product is so great, and the elasticity of it so much augmented by the caloric suddenly disengaged, that the mere resistance of the atmosphere gives rise to a loud noise. This forms what is named Detonation. It is not only produced by heat, but, with regard to some substances, by friction, or percussion.

The last general case of the combinations of oxygen to be noticed, is that where it is transferred from one body to another, without being accompanied by the phenomena of combustion. Thus the acids contain oxygen. In acting on an inflammable substance or a metal, they often yield this oxygen. Water, which is a compound of oxygen, sometimes affords it to other bodies; and the presence of an acid often favours this, or causes the water

to be more easily decomposed. In such cases, there is no great elevation of temperature, partly because the oxygen existing in these compounds has been deprived of the caloric peculiar to it in the aërial form, and partly as the substance evolved from the decomposition of the acid or the water, and which is usually gaseous, absorbs much of the caloric that would otherwise be rendered sensible. Neither is there in general any evolution of light: if evolved it is either not sensible from the slowness of the process, or else it passes into combination with the base with which the oxygen had been combined.

The combination of oxygen with a body, whatever may be the phenomena attending it, is named in general its Oxidation or Oxygenation, or, according to the nomenclature proposed by Mr Chenevix, Oxidizement or Oxygenizement. The result of it is, the formation of compounds which possess some common properties, and agree to a certain extent in the chemical agencies they exert. Hence they admit of some general observations.

Of these compounds some have a sour taste, are capable of reddening the vegetable colours, and of combining with the alkalis, so as to neutralize the alkaline properties. A substance possessed of these properties is named in chemical language an Acid. There are a number of Acids, and these in general, so far as they have been analyzed, contain oxygen. Hence this element is considered as the principle of acidity, from which indeed its name is derived.

Acidity, however, is not the invariable result of the combination of oxygen. The products of these combina-

tions are often destitute of any acid property. It is convenient to have a term to denote this class of compounds, and in the modern nomenclature they are denominated OXIDES.

Oxides and Acids, then, are two orders of compounds, under which are arranged all those substances that result from the combination of oxygen with other bodies. Acids are distinguished by the possession of certain common properties just now enumerated. Oxides have scarcely any common qualities by which they are distinguished; the distinction being rather negative, or denoting that the compound has no acid power. The alkalis and earths are now to be regarded as oxides, and the most distinguishing property common to them, and likewise to all the metallic oxides, is that of neutralizing the properties of acids. But there are likewise oxides to which this property does not belong. The word oxidation or oxidizement is used, in strict propriety, to denote that combination of oxygen where the resulting compound is not an acid, but an oxide. Oxygenation or oxygenizement is a more general term, expressing every combination of oxygen.

Many substances are capable only of oxidizement. Thus the greater number of the metals are capable of combining with oxygen. These compounds are generally oxides; nor, with the exception of two or three metals, by any addition of oxygen, can they be made to acquire any acid property. Hydrogen unites with oxygen only in one proportion, and forms water, which is not acid.

There are other inflammable substances, again, which are capable of combining with oxygen, forming in one pro-

portion an oxide, and in another an acid. In general, the first degree of oxygenizement forms an oxide, and this by combining with a larger proportion of oxygen forms an acid. Thus nitrogen, united with nearly two parts of oxygen, forms a substance, which having no acid property, is an oxide of nitrogen, while, united with four parts of oxygen, it forms an acid compound. The case is the same with a number of other bodies. Again, there are some which appear to form acids even in the first stage of oxygenizement; at least their existence in the state of oxide is doubtful. But, in all those substances which, by combining with oxygen in different proportions, produce both oxides and acids, the oxide is invariably the product of the first stage of oxygenizement, and the acid results from the addition of a larger proportion of oxygen. In some cases, the same substance too is susceptible of different degrees of oxygenizement, so as to form two acids different in their properties from each other; the one, from the larger proportion of oxygen, being usually the most energetic in its action.

Mr Davy has lately advanced the proposition, that there is another principle productive likewise of acidity different from oxygen,—an opinion which will be considered under the general observations introductory to the history of acids.

BOOK II.

OF WATER AND ITS BASE.

If any ponderable substance can, from general reasoning with regard to its powers, be considered as an element, water may perhaps best claim this distinction. It is the substance which exists in largest quantity in nature, and we can trace its agency in almost all the transmutations to which matter is subject. Hence, in nearly every system, both of ancient and modern philosophy, the elementary nature of water has been admitted as a leading principle.

The more rigorous researches of Modern Chemistry have been supposed, however, to establish its composition. It was observed, that in the combustion of a peculiar species of inflammable elastic fluid, Hydrogen Gas as it is now named, water is the only sensible product; and that the quantity of it which appears is equal to the quantity of this inflammable gas, and of the oxygen gas which are consumed in the combustion. And again, when substances having a strong attraction to oxygen are made to operate on water, they are found to have received this principle; a portion of the water disappears, and hydrogen gas is produced. It appeared to follow from these facts, in conformity to the principles which regulate chemical in-

duction, that water is a compound of these two gases. This conclusion was accordingly received without reserve. Some doubts have lately been suggested with regard to it, but until these are supported on better evidence, water may be regarded as a compound, and hydrogen as its base.

CHAP. I.

OF HYDROGEN.

Hydrogen exists when uncombined in the aërial form. Being disengaged in various common chemical processes, and from its property of inflammability being more easily recognised than the other elastic fluids, it was imperfectly known to the older chemists. Cavendish first clearly demonstrated its distinct existence and characteristic qualities, under the name of Inflammable Air. It has received the denomination of Hydrogen from being regarded as the base of water.

It is always obtained from water, subjected to the action of substances which attract oxygen. Thus, if watery vapour be passed over iron at a red heat, hydrogen gas is procured, and the iron becomes oxidated. If the resulting affinity of an acid be introduced, its production is more rapid, and takes place at a natural temperature. This is the process, therefore, that is generally followed. One part

of iron or zinc in fragments, is put into a bottle with a bent tube adapted to it, and two parts of sulphuric acid, diluted with five times its weight of water, are poured upon it; hydrogen gas is rapidly disengaged. The agency of the acid in promoting the decomposition is somewhat obscure, but, so far as any explanation can be given, it may be classed as an example of what Berthollet names Resulting Affinity; the acid, the metal, and the oxygen of the water, exerting mutual forces of attraction, which prevail over the single attraction of the oxygen to the hydrogen: hence the three former combine, while the last being separated from its combination with the oxygen, assumes the elastic form.

Hydrogen gas is the lightest of all the elastic fluids, and the lightest substance therefore whose gravity we can ascertain. In its usual state, when collected over water, it is about 10 times lighter than atmospheric air. When freed as much as possible from the water it holds dissolved, it is nearly 13 times lighter, or the specific gravity of water being 1000, that of pure hydrogen is 84. It is from this levity that it is employed in the construction of balloons. When free from water it is inodorous, but when humid it has a slight smell.

Inflammability is the property which, next to its great rarity, eminently distinguishes hydrogen. It kindles on the approach of an ignited body when in contact with the air; if previously mixed with twice its volume of atmospheric air, it explodes when kindled; with oxygen gas its explosion is still more violent. Water is the only sensible product of its combustion.

From this inflammability hydrogen gas has been ap-

plied to the purpose of eudiometry, a given volume of it being introduced into the tube, Fig. 22. with a measured quantity of the air submitted to trial, and inflamed by the electric spark. The diminution of volume indicates the quantity of oxygen that had been contained in the air, 100 measures of oxygen combining with rather less than 200 measures of hydrogen. Thus, 60 measures of hydrogen gas exploded with 100 of atmospheric, leave a residual gas equal to 100 measures, the 21 of oxygen in this portion of air having combined with 39 of hydrogen. Though a eudiometrical method of sufficient delicacy from the great reduction of volume, it is rather troublesome in the execution, and more simple methods are therefore generally preferred.

Hydrogen gas proves fatal to animal life when respired, apparently, however, not by any positively deleterious power, but merely by excluding oxygen: hence it can be breathed for a few inspirations; and when diluted with a portion of atmospheric air, can be breathed longer with safety. It does not, like some of the other elastic fluids, prove noxious to vegetable life; some plants even absorb it; and there are observations which appear to prove, that it can, to a certain extent, supply the place of light in supporting vegetation.

Hydrogen gas is not sensibly absorbed by water, at least unless the water has been previously freed from the atmospheric air it holds dissolved; 100 cubic inches of it then take up, according to Henry's experiments, 1.5 of the gas; by applying strong pressure, the water may be made to absorb one-third of its volume.

Hydrogen enters into chemical combinations with other substances, principally with those that are inflammable, as sulphur, phosphorus and carbon; it also dissolves some of the metals. With oxygen it forms water, with nitrogen ammonia; and it is an abundant ingredient in the vegetable and animal products.

It is disengaged by some natural processes, though not pure. Thus, holding carbon dissolved, it rises sometimes from stagnant water in which vegetable matter is diffused; and in a similar state of composition it is collected in mines, forming what has been named Fire Damp. It has been supposed, that from its levity it may be accumulated in the upper regions of the atmosphere, and that some of the phenomena of meteorology may be connected with its action.

The recent discoveries in chemistry have suggested some interesting speculations with regard to the nature of hydrogen,—a singular fact having been established, which leads to the conclusion, that its base or gravitating matter is of a metallic nature. The substance named Ammonia is a compound of hydrogen with nitrogen. When this is placed in contact with quicksilver, negatively electrified in the galvanic current, the quicksilver increases rapidly in volume, acquires consistence, and becomes at length a soft solid. These are changes strictly analogous to what it would suffer from the addition of metallic matter, and they can scarcely be supposed to arise from any other cause. They lead to the conclusion, therefore, that the ammonia, in the decomposition it suffers in the galvanic circuit, has yielded metallic matter to the quicksilver; this

must be derived either from the nitrogen or the hydrogen, which are the elements of the ammonia. Hydrogen being inflammable, may be supposed, with more probability, to be allied to metals, and the results therefore afford some ground for the conclusion, either that its gravitating matter is metallic, in other words that hydrogen is a metal in the gaseous form, or that it is a metal in some state of combination, perhaps in an oxidated form. Or, from the ultimate relation which appears to exist between hydrogen and nitrogen, both may be compounds of the same metallic base.

Mr Davy has remarked, that even a different view, extending still farther the relations of hydrogen, may be presented; that it may be, as was formerly maintained in the discussion of the antiphlogistic theory, the common principle of inflammables and of metals, forming them, when combined with unknown bases, and thus acting in opposition to oxygen. This receives some support from the apparent relations of those principles to the different electrical states. "Oxygen is the only body which can be supposed to be elementary, attracted by the positive surface in the electrical circuit; and all compound bodies, the nature of which is known, that are attracted by this surface, contain a considerable proportion of oxygen. Hydrogen is the only matter attracted by the negative surface, which can be considered as acting the opposite part to oxygen: may not then the different inflammable bodies, supposed to be simple, contain this as a common element?" But to these speculations, as Mr Davy has justly added, not much importance can be attached.

"The age of chemistry is not yet sufficiently mature for such discussions; the more subtle powers of matter are but just beginning to be considered; and all general views concerning them must as yet rest upon feeble and imperfect foundations."

CHAP. II.

OF WATER.

The composition of water has been inferred both from analysis and synthesis. When hydrogen gas is burnt, an operation in which of course oxygen is combined with it, water is the only sensible product; and when water is acted on by substances capable of attracting oxygen, these are oxidated, water disappears, and hydrogen gas is evolved. From these facts, the conclusion was drawn nearly at the same period by Cavendish and Watt, that water is a compound of hydrogen and oxygen; and the experiment, of forming water by burning hydrogen gas, was executed by the former philosopher on a considerable scale. It has since been often repeated, and with the utmost attention as to the proportions and the accuracy of the results.

This was necessary, not only from the importance of the question in its relations to chemical theory, but also as

some circumstances were found connected with the experiment, which required to be elucidated. In particular, it was observed, that an acid is frequently formed alongst with the water; and some were disposed to conclude, that this is the real product, and that the water is only adventitious, being the moisture deposited, which had been held dissolved by the gases. The repetition of the experiment, however, discovered the origin of this acid. It was found to be generally the nitric: this acid is a compound of oxygen and nitrogen, and had therefore been formed from nitrogen, which had been mixed with the gases, and from which indeed it is difficult to procure them entirely free. Sometimes the acid appeared to be the carbonic, and this had obviously been derived from a small portion of carbon held dissolved by the hydrogen, derived from the materials from which it had been obtained. When these sources of fallacy are guarded against, the water formed in the combustion is perfectly pure, and the weight of it amounts exactly to the weight of the hydrogen and oxygen gases consumed. This has been established by repeated experiments, made on a large scale, and with the greatest care.

The composition of water has also been established by analytic experiments. When transmitted over iron at a red heat, the iron is oxidated, and hydrogen gas is disengaged. And it has farther been proved, that the quantity of hydrogen, added to the increase of weight which the iron gains, corresponds with the quantity of water which disappears.

From these experiments, synthetic and analytic, the

proportions of the two gases which unite to form water have been determined. Excluding fractional parts, which, from the nature of the experiment, cannot be of any importance, they may be fixed at 15 of hydrogen by weight, and 85 of oxygen.

The action of electricity affords a mode of resolving water into its constituent gases, and of combining these again so as to reproduce it. When an interrupted electrical discharge, from a coated jar, is transmitted by wires, placed at a short distance, through a column of water, there is a production of aëriform fluid; and when from repeated discharges this has accumulated in sufficient quantity to be examined, it is found to consist of oxygen and hydrogen gases: hence, when the electric spark is taken in it, it immediately disappears with inflammation; the two gases being combined, and water again formed. The experiment, as a proof of the composition of water, is so far satisfactory, as the results are obtained without the intervention of any other ponderable matter.

Lastly, the action of electricity, in the form of galvanism, has afforded similar results, connected also however with peculiar phenomena, which require to be stated more particularly, as it is from them that doubts have been suggested, whether the theory with regard to the composition of water is just.

If in a quantity of water in a glass tube a wire connected with the positive side of a galvanic battery, and another wire from the negative side be inserted, employing metals which are not susceptible of oxidation, as gold or platina, and bringing the extremities of the wires to the

distance of about half an inch from each other, a stream of gas immediately arises from each, and this continues while the galvanic action is kept up, until, by the accumulation of elastic fluid, the water is depressed beneath the extremity of the upper wire. When this aërial fluid is examined, it is found to consist of oxygen and hydrogen, in the proportions which form water, and by transmitting the galvanic spark through it, it is again converted into water.

In this experiment is presented a phenomenon which appears at first view singular. If the evolution of elastic fluid arise from the decomposition of water, it might be expected that the elements must be evolved together, and that of course a stream of oxygen and of hydrogen gases shall arise from each wire. On making the experiment, however, so that the gas from the wires shall be obtained separate, as is easily done by inserting each in a separate tube, either placed in the same vessel of water, as represented Fig. 25. or even connected only by a humid conductor, or by the interposition of certain liquids, it is found, that the gas from the one wire, that connected with the positive side of the galvanic battery, is oxygen, that from the other or negative side is hydrogen, and each is perfectly pure, if care has been taken to free the water from the atmospheric air it holds dissolved. The elements of the water are evolved therefore at separate, and even at distant points; and the question that obviously presents itself is, what becomes of the oxygen at the wire where the hydrogen is evolved, and what becomes of the hydrogen where the oxygen is given out?

To solve this question, various hypotheses were proposed. It was supposed that water, in common with other compounds, is capable of combining with an excess of either of its ingredients, and that in this experiment it may remain with such an excess at each wire, with an excess of hydrogen at the wire where oxygen is evolved, and with an excess of oxygen at the wire where hydrogen is disengaged,—an hypothesis liable to the obvious objection, that when the portions of water are in separate vessels, connected only by a humid conductor, this must have a limit, and that the properties of the water, from such changes of composition, must soon suffer important changes. By other chemists, it was imagined, that the principles of the decomposed water are conveyed by the galvanic influence to these distant points. How this was accomplished, was never, however, very well explained; and the improbable hypothesis was even advanced, that it might be by the direct combination of the principle of galvanism either with oxygen or hydrogen. Mr Davy at length shewed, that this is merely a case of the general law by which the decompositions from galvanic influence are produced; that certain substances are, from their peculiar relations to electricity, attracted to the positive, and repelled from the negative pole of a galvanic series, while others are attracted to the negative, and repelled from the positive pole; oxygen and acids belonging to the former class, hydrogen, and in general inflammable substances, as well as alkalis and earths, belonging to the latter. When water, therefore, is submitted to the action of galvanism, the oxygen of a portion of it is, in conformity to

this law, attracted to the positive side, and the hydrogen is repelled: the reverse of this happens at the negative side, the hydrogen is attracted, and the oxygen repelled; the decomposition of the water is therefore the result, each of its elements is brought to the wire in connection with that side of the galvanic series to which it is attracted, and as it cannot enter the wire, it there assumes the elastic form. The evidence on which this law rests, has been already stated, and it affords a sufficient explanation of this phenomenon.

Some chemists, however, have proposed a theoretical view of this subject altogether different. It has been remarked, that water may not be a compound, but a simple body assuming the forms of oxygen and of hydrogen according to its electrical states. When rendered positively electrical, it will form hydrogen gas; when in the opposite or negative state, it will constitute oxygen; and when brought within the sphere of action in these forms, the two electrical states will be subverted, the equilibrium established, and water will be reproduced.

It is difficult to prove the impossibility of an hypothesis of this nature, but it forms perhaps a sufficient objection to it, that it has nothing peculiar for its support. Were water the only substance suffering such changes when submitted to galvanic action, this would afford some grounds for such a conclusion; but all compound substances suffer changes equally important; they appear under the form of new substances, or are converted into what we regard as their constituent principles. To consider these principles as the compound in different electrical states, would be an

extension of the theory extravagant and absurd, yet there is no reason why it should be limited to water, since there is nothing peculiar in its apparent production or decomposition. Its conversion into oxygen and hydrogen, by the action of galvanism, is exactly similar to the conversion of sulphate of potash into sulphuric acid and potash by the same action: the conclusion, that the water is a compound of these principles, rests precisely on the same grounds as the conclusion that the compound salt consists of the acid and the potash, and both rest on evidence as direct as can be adduced in support of any chemical fact *.

---

* Ritter, by whom this theory of water, being a simple substance appearing under the forms of oxygen and hydrogen, according to its electrical states, was maintained, has stated, that when a wire attached to the positive side of a galvanic battery is placed in water in a tube, and a wire from the negative side is placed in another portion of water in another tube, and when these are connected, not by placing them in a vessel of water, but in separate vessels connected by a metallic wire, the usual phenomena are produced, and the oxygen is evolved at one wire, the hydrogen at the other. Now, although it may be supposed, that particles of oxygen and hydrogen may be conveyed to distant points by powerful attracting or repelling forces through water, it can scarcely be conceived, that they shall be capable of being conveyed thro' the wire of metal, which in this experiment forms the medium of connection between the two portions of water; and hence the result, Ritter concludes, establishes the conclusion, that the communication merely of positive and negative electricity to water (the metallic wire in this case completing the circuit) causes it to assume these forms. Were the fact as it is stated, the conclusion would perhaps follow. I have found, however, on making the experiment, that it is a mere deception. The connecting

It was at one time supposed, that in the decomposition of water by galvanism, there is a formation of new products: a portion of acid frequently was observed to be formed at the positive wire, and of alkali at the negative wire. The origin of these, however, has been sufficiently traced. They are in general derived from the small portion of saline matter which water holds dissolved, and from which it is not even perfectly freed by one distillation, the acid of which is attracted to the one wire, the base to the other; and as these attractive powers are so strong, the most minute quantities are rendered sensible. From the same circumstance, even the containing vessel is sometimes acted on; and the atmospheric air, held dissolved by water, has some influence, its nitrogen,

---

wire becomes a galvanic one, and its two extremities becoming electrical, by what electricians have denominated position or induction, are in states of electricity the reverse of the galvanic wires in the tubes; and hence oxygen and hydrogen are evolved at their extremities, corresponding with the hydrogen and oxygen evolved at the others; the extremity of the connecting wire, for example, in the tube in which the *positive* galvanic wire is inserted, being *negative*, and giving out hydrogen, corresponding to the oxygen which appears at that wire, and its other extremity in the tube in which the *negative* wire is inserted being *positive*, and therefore giving off oxygen, corresponding to the hydrogen which appears at that wire. The effect, I have farther found, is exactly the same in the decomposition of a compound salt, acid being collected at the extremity of the positive galvanic wire, and alkali at the extremity of the negative galvanic wire in the different tubes, but the corresponding portions of alkali and acid appearing at the same time at the extremities of the connecting wire.

by combining with the nascent oxygen at the positive pole, forming nitric acid, and combining in like manner with the nascent hydrogen at the negative pole, and forming ammonia. But when these sources of fallacy are avoided, the water, Mr Davy has shewn, remains pure to the end of the experiment, and is resolved into oxygen and hydrogen alone.

Water, as a chemical agent, has qualities extremely peculiar. It affords the example of an inflammable base saturated with oxygen, forming a product which has no acidity. Besides this, though its affinities are extremely numerous, they are seldom energetic; and hence in general it combines with bodies, without materially changing their qualities, and by communicating fluidity to solids, without modifying much their chemical relations, favours their mutual actions.

It is tasteless, colourless, and inodorous. It passes to the solid state at 32° of Fahrenheit, and in doing so crystallizes, spiculæ shooting out at a certain angle, and of a prismatic form: by the continuance of the congelation, the vacuities are filled up, but the mass remains transparent, and is hard and brittle. In congealing, there is, as has been already stated, an enlargement of volume, and this expansion even takes place previous to the congelation, during the reduction of temperature, for six or eight degrees, the greatest density of water being about 40°. In the act of freezing, too, the greater part of the air which the water holds loosely dissolved is expelled.

Water passes into vapour when exposed to the atmosphere at any natural temperature, and even ice evapo-

rates, as is proved by its losing weight when suspended in the air. The transition into vapour is promoted by heat; at 212°, under a medium atmospheric pressure, water boils. Its vapour at this temperature is permanent, transparent, and invisible; when condensing, it becomes, from the approximation of the particles, opaque. It occupies 1800 times the space which it fills when in the state of water, and has a specific gravity to that of atmospheric air at the same temperature as 10 to 14. It exerts a great degree of elastic power, and its elasticity increases in a high ratio by elevation of temperature.

Water absorbs the aërial fluids, but in quantities very different, according to the force of attraction which it exerts towards them. Of some of the acid gases, it absorbs many times its own volume; of others the quantity is so inconsiderable as not to be very perceptible, unless ascertained by an apparatus adapted to shew the result. The quantities absorbed are greater as the temperature is low, down to freezing, when the cohesion of the solid, weakening the affinity, the aërial matter is expelled. They are also augmented by pressure, and, according to a very simple law stated by Dr Henry, as the result of his researches on this subject, "Water takes up in all cases, under equal circumstances of temperature, the same volume of condensed gas, as of gas under ordinary pressure." To whatever degree of density, therefore, the elastic fluid is brought by pressure, the same volume of it is still absorbed; and hence, by increasing pressure, a large quantity of the solid or gravitating matter of the gas may be forced into the water. It is singular, that water thus impreg-

nated by pressure with large quantities of the gases, which, under the mere pressure of the atmosphere it absorbs sparingly, does not suffer much change in its qualities.

This absorption of gases by water, so far at least as regards those which require pressure to cause their absorption in any sensible quantity, has been supposed by Mr Dalton to be a mere mechanical effect, the gas being forced as it were into the interstices of the water by the pressure applied. It is rather to be regarded, however, as arising primarily from the affinity exerted by the water to the particles of the aëriform fluid. This is counteracted by the elasticity of the gas, and not being strong it cannot operate with much effect. Pressure counteracts this elasticity, hence lessens the resistance opposed to the combination, and, operating like reduction of temperatnre, causes a larger quantity to be absorbed. We accordingly find, that in those cases where the exertion of an affinity by the water to the gravitating particles of the gas is undoubted, as in the example of muriatic acid gas, pressure is equally effectual in promoting the absorption: and also what is in conformity to this view, that even in those gases the absorption of which is inconsiderable, the quantities absorbed are different under the same pressure,—a difference which can only be ascribed to the different forces of affinity exerted to them by the water.

There are some important facts with regard to the relations of water to the aërial fluids in their absorption. Thus, from the affinities it exerts to all of them, however weak, if it be agitated with a mixture of two or more gases, portions of both will always be absorbed, the same as

if they were presented to it separately in their proper density; the quantity therefore being greatest of that which separately is most largely absorbed by water. Or, if water has been previously impregnated with one gas, on agitating it with another, a portion of the latter will be absorbed, and a portion of the former displaced. Hence, as water usually contains a portion of atmospheric air, in exposing any gas to an extensive surface of it, and still more in agitating any gas with it, while a quantity of this is absorbed, a portion of the air the water holds dissolved will be separated, and added to the residual gas, whence frequently sources of error have arisen in chemical experiments; oxygen gas, for example, if kept in a jar surrounded with water exposed to the air, will soon have an intermixture of atmospheric air; and indeed all gases long exposed in this manner have a similar intermixture from the water yielding its air.

Water which has been exposed to the atmosphere always contains portions of both of its constituent gases; but the oxygen appears to be absorbed in preference to the nitrogen, and in larger quantity. Hence by agitating atmospheric air with a large portion of water, or passing it repeatedly through a column of water, the greater part of its oxygen is abstracted. The presence of oxygen loosely combined in water, is usually shewn by the test of sulphate of iron; the oxide of iron which is the base of this salt, attracting this portion of loose oxygen, whence becoming insoluble, it is precipitated, and forms a yellow sediment: this precipitation seems also, however, to be in part owing to the decomposition of the salt by the affinity of the wa-

ter to its acid, aided by its quantity. The portion of air held dissolved by water is expelled with difficulty. It is in part removed by removing the atmospheric pressure by the air-pump, by strong boiling, and by freezing, but part of it is still retained. It is rather singular too that the nitrogen appears to be retained with greatest force. If, through water freed as much as possible from air by boiling, and by the air-pump, an electrical discharge be transmitted, a small portion of nitrogen is disengaged, along with the oxygen and hydrogen evolved from the decomposition of water, as Dr Pearson found in his experiments. And in freezing water which had been previously freed as much as possible from air by boiling, the air disengaged is, according to the experiments of Priestley, nitrogen, especially when the freezing of the same portion of water has been repeatedly performed. Ritter, on the contrary, has inferred from some experiments, that the air disengaged in the freezing of water is oxygen, evolved from decomposition, and that ice has therefore an excess of hydrogen. Mr Davy has more lately found, that this air is atmospheric air, and that the production of it does not take place in the unlimited manner which had been represented by Priestley, but ceases after the freezing has been repeated three or four times. Water melted from snow with the exclusion of the atmosphere, appears to be nearly free from air. Rain water, and especially dew, have, on the contrary, been supposed to be saturated with air. Spring water, besides the atmospheric air it holds dissolved, contains a portion of carbonic acid.

Water is contained in all the elastic fluids, derived ei-

ther from the materials from which they have been extricated, or that through which they have been transmitted. It exists in them in the state of vapour, probably weakly combined, and is capable of being condensed, in part at least, by cold, and of being abstracted by substances exerting an attraction to it, as by sulphuric acid or lime. But even when abstracted as much as possible by the action of these substances, it has been supposed that a portion is retained by a stronger force; and there are facts which appear to prove, that in some gases at least, the quantity of this is considerable, and is essential even to their existence in the aëriform state. This is a question at present of much interest, but not easily determined.

A singular fact, from which this conclusion with regard to the existence of combined water in aërial fluids has been drawn, is, that in compounds in which these gases exist in a dry state, the gas cannot be disengaged by heat unless water be supplied. This is the case with the native carbonate of barytes or of lime; and from the former, even the carbonic acid is very imperfectly disengaged by an acid, unless it be diluted with water. From both facts it has been inferred, that water is essential to the constitution of carbonic acid gas,—an inference which may be just to a certain extent, though it is also possible that the operation of the water may be not altogether on the gas, but on the base with which it is combined, favouring its disengagement by the attraction it exerts to that base.

Another fact in favour of the same conclusion is the disengagement of hydrogen from certain gases, when they

are submitted to the action of the electric spark, after they have been rendered as dry as possible. In some of these experiments, indeed, those where the carburetted hydrogen gases were operated on, it now appears that the fact had not been accurately observed, the phenomena whence the evolution of hydrogen had been inferred being owing to the decomposition of the gas itself; but there are others free from this ambiguity, muriatic acid gas, for example, affording about $\frac{1}{11}$ of its volume of hydrogen gas, on being submitted to the action of the electric spark, after it has been exposed to muriate of lime to abstract its water.

The facts more recently established, with regard to the relation of muriatic acid to water, appear to prove still more clearly the necessity of water to its existence in the gaseous form. Thus Gay Lussac and Davy found, that this acid could not be disengaged from its combinations by a dry acid with the aid of heat, from muriate of lime for example, by phosphoric or boracic acid, while if water were added, it was disengaged in large quantity. The gas itself too, rendered as dry as possible, on being submitted to the action of potassium, afforded hydrogen in such quantity, that Mr Davy inferred, first, that it must contain at least one-tenth of its weight of water, and afterwards that the quantity must amount even to one-third of its weight. These latter facts may indeed admit of a different explanation on the new theory which Mr Davy has given of the constitution of muriatic acid; but that theory can scarcely be regarded as established; and the facts are

on the whole favourable to the conclusion, that in gases, and particularly in those the gravitating matter of which has a strong attraction to water, a considerable portion of this fluid exists, and is necessary to their transition to this state. The still more singular fact appears even to be established, that it is necessary to the development of their acid powers. This, however, will form a subject of consideration under the history of muriatic acid.

Water is the general solvent of saline substances, and in those of them which crystallize, it is always retained, forming a part of the substance of the crystal. It is capable of dissolving the earths, some of them in considerable quantity, particularly barytes and strontites; the others more sparingly. Even those earths and stones which it cannot dissolve, it wears away and reduces to a state of extreme division, partly by attrition, and partly by its chemical powers. Hence it acts even on glass, especially when aided by a high temperature,—a fact which at one time gave rise to the opinion that it is convertible into earth, a portion of earth being always left when it is distilled from glass vessels.

Water, though incapable of combining with the metals, exerts a chemical action upon them, affording to several of them oxygen at the temperature of ignition; and at a natural temperature, aided by atmospheric air, oxidating or corroding others. At a high temperature it is decomposed by charcoal and sulphur, which receive from it oxygen.

Water is a solvent of many other substances. Few of the animal or vegetable products are insoluble in it, and all

of them are affected by it as a chemical agent, receiving from it oxygen, or the re-action of their constituent principles being promoted by the fluidity it communicates, so as to give rise to spontaneous decomposition.

From the extensive solvent power of water, it is scarcely ever met with pure in nature. Every kind of spring or river water is impregnated with saline and earthy bodies of different kinds. Spring water contains, according to Bergman, carbonate of lime, muriate of lime, and muriate of soda; river water contains carbonate of lime, muriate of soda, and each of these also sometimes a little alkali. Well-water, besides these, contains always a portion of sulphate of lime, the presence of which is the cause of the quality in waters termed *Hardness*. Rain or snow water is freer from these foreign substances, but is not perfectly pure, as it affords a trace of muriate of soda and muriate of lime. Water is freed from these substances by distillation; and for any chemical process in which accuracy is requisite, distilled water must be used.

BOOK III.

OF ALKALIS AND THEIR BASES.

Three substances possessed of certain common properties have been long classed together by the chemists, under the name of Alkalis. They are soluble in water; their taste is acrid; and when applied to animal matter, they erode or dissolve it; they change the blue and purple colours of vegetables to a green, the yellow they change to a brown; they combine with oils and fats, forming soaps; and they unite with the substances which belong to another class, the acids, neutralizing their characteristic properties, so that in the compound which is formed, when the due proportion is observed, the presence of the acid or of the alkali cannot, from any remaining property of either of them, be recognised. The three alkalis are named Ammonia, Soda, and Potash, (or what, for similarity of termination, would be preferable, Potassa.) The first existing when uncombined in the aërial form, and being even when combined with water easily volatilized, has been named Volatile Alkali; the other two, though they are volatilized at a red heat, yet still having comparative fixity, are denominated Fixed Alkalis.

The most important and characteristic property of the alkalis is that displayed in their relations to the acids,

drogen, and that it is therefore the communication of this element, not the abstraction of oxygen, which takes place in their production.

Though the alkalis, earths, and metallic oxides have been connected by these discoveries, there still remain, perhaps, sufficient reasons to arrange them as distinct orders; and in the present state of chemistry, it is even necessary that this arrangement should be adhered to. The bases of the alkalis and the earths, though they may be regarded as metallic, are very different from the common metals, both in their physical and chemical properties; and except in the leading character of combining with the acids, the alkalis are very different in their qualities from the metallic oxides, and are much more active in their chemical relations. The earths approach nearer to the metallic oxides, and form the series intermediate between them and the alkalis.

Several of the earths, particularly barytes and strontites, approach so nearly to the alkalis in their properties, that it has been proposed to transfer them to this class. They are still, however, on the whole, more strictly connected with the other earths: if the entire series is to be subdivided into two orders, it could not be done with more propriety, than in conformity to those already established; and the alkalis may be regarded as associated and distinguished by their much greater solubility in water, and affinity for it; by their solubility in alkohol; by their greater fusibility and volatility, and in general by their greater activity as chemical agents.

CHAP. I.

OF AMMONIA AND ITS BASE.

THIS alkali, obtained by indirect processes, was known to the older chemists only in its combination with water, forming the liquid which, from its volatility compared with the other alkalis, was denominated Volatile Alkali. Dr Priestley first shewed, that a permanently elastic fluid can be procured from it by a moderate heat, and that this is the alkali in its pure form.

In the progress of pneumatic chemistry, several facts were observed, proving the composition of ammonia. Priestley found, that on taking the electric spark in it, or on transmitting it through an ignited earthen tube, the volume was much enlarged, and its properties were entirely changed; it was no longer absorbed by water, and was highly inflammable. By heating certain metallic oxides in the ammoniacal gas, he farther found, that they are reduced to the metallic state; a little water appeared to be produced, and the residual gas was nitrogen. Scheele, too, observed the decomposition of ammonia, and the production of nitrogen, particularly in the detonation of fulminating gold, a substance composed of ammonia and oxide of gold.

Berthollet, reviewing and comparing these experiments,

was led by them to institute others, in which ammonia was decomposed; and, from the whole, he inferred that it is a compound of hydrogen and nitrogen gas. From the products of its decomposition by the electric spark, he concluded, that 100 parts of it contain by weight 80.7 of the nitrogen with 19.3 of hydrogen. With this the results of the analytic experiments made by Mr Davy at a later period, almost agree; the proportions he assigns being 80 and 20. Both Dr Henry and Mr Davy find, that when 100 measures of ammonia are decomposed by the electric spark, 74 measures of hydrogen and 26 of nitrogen are obtained, which correspond to the above proportions.

The composition of ammonia is not easily established by synthesis, the elasticity of the two gases being an obstacle to the exertion of the mutual affinity of their gravitating matter, so that when mixed together they cannot be combined, even by the agency of the electric spark. It had been observed, however, that in some cases of chemical action, ammonia is evidently formed, or is evolved, though it does not pre-exist in the materials. This production of it was known to take place in the action of nitric acid on tin; and the theory of its production, as well as the principle on which it depends, were ascertained by Austin. Tin being a metal having a great avidity to oxygen, it decomposes when acted on by nitric acid, both the acid itself and the water the acid contains attracting the oxygen of both. The nitrogen of the one and the hydrogen of the other are evolved: and being presented to each other in the moment of their evolution, and before they have become elastic, (in their *nascent state*, as it has been

named), their mutual affinity is exerted with effect, and they combine. Dr Austin farther found, that it was sufficient to present hydrogen in its nascent state to nitrogen gas to form ammonia, this result being obtained when iron-filings moistened with water are confined in a tube with nitrogen gas over quicksilver. The reverse experiment, however, that of presenting nascent nitrogen to hydrogen gas, was not successful, probably from the great rarity of hydrogen in its gaseous form.

The discovery of the existence of oxygen, as a constituent principle of the other two alkalis, potash and soda, obviously suggested the suspicion, that it probably also exists as an element in the composition of ammonia, and if the experiments on the analysis of ammonia be examined, it will appear that they do not preclude the possibility of this; for when it is resolved into hydrogen and nitrogen gases, a small portion of oxygen might be mingled with these, and not be detected from the manner in which the experiments were made; or by combining with a portion of the hydrogen, it might be disguised in the state of water. On the discovery, therefore, of the existence of oxygen in the composition of the fixed alkalis, it became an object of importance to determine whether it does not also exist in the composition of ammonia.

It appeared to be established by Mr Davy's experiments that it does. On heating charcoal in ammoniacal gas, rendered as dry as possible, carbonic acid (a product formed by the combination of charcoal with oxygen) was formed. By transmitting ammoniacal gas repeatedly over iron-wire in a platina tube at a red heat, the pre-

sence of oxygen was rendered apparent, both by the oxidation of the iron, and the deposition of water. And, lastly, in resolving ammonia into hydrogen and nitrogen gases, by the agency of the electric spark, and estimating the quantities of these by weight from their volumes, there was found a deficit of nearly $\frac{1}{11}$ of the ammonia employed, probably from the disappearance of a portion of oxygen, combining partly with the platina wires employed in the experiment, and partly with hydrogen forming water. From these experiments Mr Davy inferred, that the proportion of oxygen in the composition of ammonia may be equal to seven or eight parts in the hundred, or may even be larger.

The experiments of other chemists have not, however, confirmed these results. Dr Henry, submitting ammonia to analysis by the action of electricity, has, when the due precautions have been observed, been unable to obtain any indications of oxygen; it is resolved into hydrogen and nitrogen alone. The same conclusion has been drawn by Berthollet from his experiments. And, more lately, Mr Davy, repeating his experiments, has not obtained results favourable to the conclusion, that oxygen is evolved in the decomposition of ammonia, but rather establishing the reverse, that the products are hydrogen and nitrogen. In either of these, however, oxygen may be an element, as has been already stated; and on the theory that it is the principle productive of alkalinity, this supposition obviates the anomaly, which ammonia would otherwise present.

The analogy in chemical constitution between ammonia and the other alkalis has been under another point of

view, that which relates to its base, confirmed by the interesting discovery by Berzelius and Pontin, noticed under the history of hydrogen, that metallic matter is obtained from it by the action of galvanism. This matter cannot be procured by itself: it is necessary to introduce the operation of another substance which may combine with it, and this is done by placing quicksilver in the galvanic circuit with a solution of ammonia, or with an ammoniacal salt, carbonate or muriate of ammonia. On completing the circuit, by connecting the positive and negative wires of the galvanic battery with the ammonia and the quicksilver, the latter soon undergoes changes indicating the communication to it of metallic matter. It increases in volume, becomes less mobile, and this continuing, it is at length enlarged to four or five times its original volume, and becomes a soft solid. This change is evidently analogous to amalgamation; and that the metallic matter producing it is derived from the ammonia, is apparent, not only from the circumstances of the experiment itself, but farther, from the fact, that when the amalgam is exposed to the air or dropt into water, ammonia is reproduced. These experiments were confirmed by Mr Davy: they are indeed easily performed, requiring no powerful battery: and Mr Davy farther found, that quicksilver suffers a similar change when ammonia in contact with it is subjected to the powerful de-oxidating influence of the metallic bases of either of the other alkalis.

This metallic matter must be regarded as the base of ammonia, and as such it has been named Ammonium. Whether it is derived from the hydrogen or nitrogen into

which ammonia is resolvable, or from both, or whether these gases are different forms or combinations of it, remains at present unknown; but the discovery sufficiently confirms the analogy between this and the other alkalis.

Ammonia is always procured by indirect processes. Its ultimate source is usually from the decomposition of animal matter, of which its constituent principles are elements, and which, in the new combinations taking place in that decomposition, unite so as to form it. It is thus obtained abundantly in the distillation of bones and other animal substances. Procured in this way, however, it is always impure, and the chemist therefore usually avails himself of a salt, containing it prepared on a large scale for different purposes in the arts, the muriate of ammonia, or sal-ammoniac of commerce, from which it is easily obtained pure. This salt consists of muriatic acid, combined with ammonia. On mixing it with two parts of slaked lime, the pungent smell of ammonia is immediately apparent; and on applying heat to the mixture in a retort, there is an abundant production of elastic fluid, consisting of the ammonia in this form, the lime combining with the muriatic acid of the compound salt, and the ammonia being disengaged. The ammoniacal gas is received over quicksilver, as it is instantly absorbed by water.

Ammonia, in the state of gas, has an odour extremely pungent, and is so acrid as to inflame the skin. It is one of the rarest of the elastic fluids, its specific gravity being to that of atmospheric air as 600 to 1000.—100 cubic weigh 18 grains. It is permanently elastic at natural temperatures, but when exposed to a cold —56° of Fahren-

heit, it is condensed into the liquid state,—a condensation facilitated probably by the operation of the water which it may hold dissolved. The gas extinguishes combustion; it is itself slightly inflammable, the flame of a taper partially introduced into it being enlarged, and when it is previously mingled with atmospheric air it burns with a slight lambent flame, and when kindled in mixture with oxygen gas burns more strongly. When transmitted through an ignited tube, or submitted to the action of the electric spark, it is decomposed.

Ammoniacal gas is largely and rapidly absorbed by water; the water, under a mean atmospheric pressure and temperature, taking up rather more than one-third its weight of the gas. Ice immediately liquefies in it, at the same time condenses it, and this is accompanied by the production of cold. Its solution in water is of inferior specific gravity to pure water, being, when concentrated, not more than 9054. The gas is expelled from it by an elevation of temperature; by intense cold the solution is congealed without the ammonia being separated: the congelation takes place at —40°: and at —58° it loses all smell.

It is under the form of the watery solution that ammonia is usually employed as a chemical agent. The solution is prepared by connecting a retort of green glass with the mixture of muriate of lime and ammonia in the proportions already stated, and with about twice their weight of water, with the bottles of Woolfe's apparatus containing water. Heat is applied to the retort by the medium of a sand-bath: the lime combines with the muriatic acid, the ammonia is expelled, and is condensed partly by the water

that distils over from the retort, and partly by the water in the bottles of the apparatus through which it is transmitted. On a large scale, the distillation is carried on from an iron-still containing the muriate of ammonia and lime dry, to which the fire is directly applied, the still being connected with a spiral tin tube placed in a refrigeratory, and with the extremity of which a series of globular receivers is likewise connected. When properly prepared it is colourless, and has the pungency of the ammonia unaccompanied with any fetor.

Ammonia has been supposed to be inferior to the other two alkalis in alkaline power, as they decompose the compounds it forms with the acids. This, however, is probably owing to its volatility; and as a given weight of it neutralizes larger quantities of the acids than the same weight of the other alkalis do, it follows, from Berthollet's views of the strength of chemical affinity, that it is even superior in power. From the inferior concentration, however, of its solution, it acts less strongly on a number of substances; it combines rather less intimately with the oils, and it does not dissolve the earths.

CHAP. II.

OF POTASH AND ITS BASE.

THIS alkali has long been employed in a state of greater or less purity as a chemical agent, and has been distinguished by various appellations. Being usually procured from the combustion of vegetables, it received the name of Vegetable Alkali. As it is the base of the impure alkaline salt, the potash of commerce, it has been named Potash. The term Potassa has been received as the Latin appellation, and would be preferable even in our language, as similar in termination to the names of the other alkalis, and as different from the term applied in commerce to a substance containing only the alkali in an impure form: but that of Potash appears to be established by general use.

Potash had sometimes been suspected to be a compound substance, but these conjectures rested only on remote analogies, and nothing was truly known with regard to its composition previous to Mr Davy's discovery of it. Guided by the principles which he had established with regard to the decompositions which galvanism produces, he submitted it to the action of this power in sufficient intensity, and obtained its base,—a substance before altogether unknown, possessed of very singular properties, and which has led to the discovery of others equally peculiar.

The decomposition of potash by galvanism is most easily effected by placing a small piece of it slightly moistened, in a platina cup, in connection with one extremity of a galvanic battery. On establishing the communication with the other side by a wire of platina, an effervescence is excited at the surface of the potash at the positive side, owing to the disengagement of elastic fluid, accompanied with the liquefaction of the potash; while at the surface in communication with the negative side, globules appear having metallic lustre, and in mobility similar to quicksilver. The elastic fluid disengaged, Mr Davy found, is oxygen gas; the metallic globules are the base with which the oxygen had been combined.

This analysis of potash Mr Davy confirmed by synthesis. On exposing the metallic-like matter to atmospheric air, its lustre is diminished, a white crust soon forms upon it, which is potash, and this is accompanied with an absorption of oxygen. On heating it in oxygen gas it entered into vivid combustion; solid potash was likewise produced, and a portion of the oxygen consumed. Or, lastly, on dropping it into water, an immediate disengagement of hydrogen takes place, the metallic matter disappears, and a solution of potash is obtained. From these experiments, both analytic and synthetic, the conclusion appears necessarily to follow, that potash is a compound of this metallic matter and oxygen, since it is resolved into them, and is re-produced when they combine. The proportions have been estimated by Mr Davy to be, at a medium, 85 of base, and 15 of oxygen.

A confirmation of this discovery, extremely important,

as excluding any suspicion that might have been entertained that galvanic action is essential to these changes, was soon after the publication of Mr Davy's experiment made by the French chemists, Gay Lussac and Thenard, potash having been decomposed by them by the action of iron,—an experiment which has been often repeated with success. Clean iron-filings are put into an iron tube, bent so that the filings shall lie in the curvature towards the middle of the tube, and be raised to the necessary heat by being placed in a small furnace. To one extremity of the tube is adapted, by grinding, a smaller one having a stopper inserted at its open extremity, and containing a quantity of pure potash; when the iron-filings are raised to a white heat, this potash is liquefied by applying to it the heat required, and it is allowed to run through a small aperture on the filings. It is then decomposed, the iron attracts its oxygen, and the metallic matter, which is its base, is sublimed to the other extremity of the tube, which is kept cold, so that it shall be condensed. A little hydrogen gas is disengaged during the process, apparently derived from the water contained in the potash, and is allowed to escape by a tube of safety connected with the tube. The metallic matter adheres in brilliant plates to the sides of the extremity of the large tube; it is similar to that obtained from the decomposition of the alkali by galvanism, but is a little heavier, probably from a slight alloy of iron. Potash has also been decomposed by charcoal.

To the substance obtained in these experiments, the base of potash, Mr Davy has given the name of Potassium. The following are its principal properties.

It appears in the form of globules, having metallic lustre and opacity at the temperature of 60, very similar in appearance to those of quicksilver, but rather less mobile. At 70° the mobility and fluidity are greater, and at 100 it is completely liquid, so that the globules run easily together. At 50 it becomes solid, is similar in appearance to silver, and is malleable; at 32 it is hard and brittle. Though it resembles the metals, however, in opacity, lustre, and other properties, it differs from them remarkably in density: in this property it is inferior even to water or alcohol; when liquid it does not sink in naphtha, the specific gravity of which is .77: in its solid state it is rather heavier, but still, even at 40, it floats in this liquid; its specific gravity, therefore, is probably not more than 6, water being 10.

Potassium, though so remarkably affected by heat, is not very volatile; it requires a temperature approaching to ignition to volatilize it. At temperatures inferior to this it combines with oxygen slowly, and without any sensible combustion; but, when heated to the point of volatilization, it burns vividly with intense heat and light. It appears to combine with different proportions of oxygen; for, when slowly heated in a quantity of oxygen not sufficient to saturate it, the oxygen is absorbed, and a substance is formed of a greyish colour, consisting partly of potash, and partly of potassium in a low degree of oxidation. This, when heated in the air, or moistened with water, is converted entirely into potash.

From its avidity to oxygen, potassium decomposes water with rapidity, producing explosion with flame, and being converted by oxygenation into potash. Placed on ice

it burns with a bright flame melting the ice. It attracts oxygen with similar rapidity from the mineral acids, and burns; and so susceptible is it of oxidation, that it is difficult to preserve it unchanged.

It unites with inflammable substances. When heated in hydrogen gas, it diminishes in volume: and the gas, on being mingled with atmospheric air, explodes with the production of alkaline fumes. It unites with phosphorus; and if the air has been excluded, the compound has the appearance of the metallic phosphurets. When heated with sulphur, under the vapour of naphtha, they combine rapidly with the evolution of heat and light, and form a substance of a grey colour, with the lustre and appearance of artificial sulphuret of iron.

It also combines with the metals, and forms compounds having metallic properties which absorb oxygen from the air and decompose water, potash being formed, and the metal separated unchanged. Its action on quicksilver is singular. They instantly combine with the evolution of more or less heat: the potassium in a minute quantity adds to the consistence of the quicksilver, and diminishes its mobility: when the quantity is about $\frac{1}{70}$ of the weight of the quicksilver, the amalgam is soft and malleable: in a quantity a little larger it renders it solid, and nearly similar to silver in colour. When it amounts to about $\frac{1}{10}$ of the weight of the quicksilver, the alloy is hard and brittle. The fluid amalgam dissolves all the metals, even those with which quicksilver alone does not combine. Compounds of the metals with potassium are likewise formed by heating an excess of it with the metallic oxides, one portion of it

abstracting oxygen and forming potash, the other uniting with the reduced metal. From this action it acts on glass, reducing the oxides of iron and lead which it contains, and forming potash, which dissolves the glass.

Though this substance has not the property which has been regarded as most characteristic of the metals, that of great density, it can scarcely but be regarded as metallic, as it has the peculiar physical qualities belonging to the class, opacity, lustre, and malleability: and in its chemical relations it displays properties similar to those of other metals,—combining with oxygen, uniting with inflammables, and with the metals themselves, forming compounds which retain the general metallic qualities.

Gay Lussac and Thenard, in conformity to the theory they have advanced with regard to the metallization of the alkalis, consider potassium as a compound of potash and hydrogen, the latter element being afforded in its formation by the water which the alkali contains. The opinion does not rest on any conclusive argument, and the discussion of it merely as a possible hypothesis, would, in the present state of the inquiry, be premature.

Potash, of which this substance is the base, is usually procured from the combustion of land vegetables, the process being carried on in those countries which abound in wood; the ashes remaining after the combustion being lixiviated, the liquor affords, on evaporation, saline matter, which, when exposed to heat, forms a solid white mass. This consists of various salts, principally of potash, combined with carbonic acid, partly also of potash combined with sulphuric and muriatic acids, together with

siliceous earth, oxides of iron and manganese, and occasionally other impurities. It has not been well determined, whether the alkali is produced by the combustion, or whether it pre-exists in the vegetable matter, and is merely evolved. It is obtained in different quantities from different vegetables: the harder woods afford more than those that are spongy, shrubs more than trees, herbaceous plants a quantity still larger, and even different parts of the same plant give different proportions of it, the leaves, from a given weight, yielding more than the branches, and the branches more than the trunk.

Potash is sometimes procured from other sources, and in a state rather more pure, as from the decomposition by heat of the salt named Tartar, or from the deflagration of nitre with charcoal, this alkali being the base of these salts.

Potash, as obtained by all these processes, is combined with carbonic acid. To abstract this, the saline matter, the Sub-Carbonate of Potash as it is named, is mixed with twice its weight of recently slaked lime, and as much water as is necessary to give the consistence of a thin paste: this is put into a glass funnel, the tube of which is obstructed with a piece of linen; the mass of lime soon subsides, so that the liquid portion filtrates through it very slowly, and water is occasionally added, as the filtration proceeds, until a quantity of liquid has passed through ten times the weight of the sub-carbonate of potash employed. The lime in this process attracts the carbonic acid, and, from the large quantity employed, and the slowness with which the water holding the alkali dissolved passes through

it, the abstraction is more complete than could be obtained by any other arrangement.

Still, though the potash is thus obtained in a state of solution nearly pure, it is not perfectly so; a little carbonic acid remains combined with it, and there may be present too small portions of sulphate and muriate of potash, originally derived from the potash of commerce, as well as a little siliceous earth. To obtain it in a state of purity, different methods have been proposed; that which is generally followed is one proposed by Berthollet. Potash is soluble in alkohol, but is insoluble when combined with carbonic or sulphuric acid. The alkaline solution, therefore, obtained by slow filtration from the mixture of subcarbonate of potash and lime, is evaporated until it become of a thick consistence, and there is then added to it an equal weight of alkohol. A quantity of undissolved matter subsides, a dark-coloured liquid floats above this, which is principally water holding dissolved potash combined with carbonic acid; a lighter coloured liquor is above this; it is drawn off, and is partially evaporated in a silver bason. On standing, it separates into two liquids of different specific gravities, the heavier being a solution of the alkali with carbonic acid, the lighter a solution of the pure alkali. The latter is poured off, and is evaporated, so that on cooling it shall either deposite crystals, or pass into an irregular crystallized mass; a small portion of residual liquor being poured off, the potash is thus obtained in a solid form.

Potash thus prepared is, if the evaporation has been carried to dryness, a substance solid, hard, and brittle, of

a white colour. If evaporated to a less extent, it crystallizes in forms which are modified by the degree of evaporation: it is thus obtained in thin plates, in slender needles, or in tetrahedral pyramids, single or double, these containing different portions of water of crystallization. They produce cold in dissolving in water, while the solid potash produces heat. Even in the driest form to which it is reduced by evaporation, and after it has been kept in fusion, the potash retains a considerable quantity of water combined with it; 100 parts containing, according to Berthollet's estimate, 14 of water. Mr Davy has observed, that the product formed by the combustion of potassium in dry oxygen gas is, from the absence of water, much less fusible than the common potash: it is the alkali in its pure form, and requires about 19 *per cent.* of water to convert it into a substance analogous to the common potash, which, even when it has been heated to redness, is a hydrate of potash.

In all these forms the alkali has a strong attraction to an additional portion of water: it imbibes it rapidly from the atmosphere, so that its surface becomes humid, and dissolves in less than its own weight of water, forming a solution dense and somewhat viscid. It is very fusible, melting at a heat of 360°; this fusibility is owing in part, however, to the water it contains. At a red heat it is volatilized. So great is its causticity, that it quickly erodes animal matter; and its alkaline powers are so energetic, that the most minute quantity of it changes the blue and purple colours of vegetables to a green.

Potash has the distinguishing alkaline property, that of combining with acids, and neutralizing the acid powers, though, as a larger quantity of it is necessary to saturate a given weight of acid than is required of ammonia or soda, it is probably inferior to them in real alkaline power.

It unites too with oils and fats, forming soaps, which, though concrete, are soft or gelatinous.

With some of the earths it combines by fusion, and others it dissolves even in the state of its watery solution.

It has little energy of action on the metals, but combines with some of their oxides. It unites too with sulphur and phosphorus, rendering them to a certain extent soluble in water, and enabling them to decompose it by attracting oxygen.

From the numerous and powerful chemical actions which it exerts, it is applied to many purposes of utility in the arts, and as it is the alkali most easily procured, it is the one most extensively used. It is thus employed in bleaching, dyeing, soap-making, the manufacture of glass and others. In medicine, it is employed as an antacid, a lithontriptic, and an escharotic.

Besides being produced in the vegetable, it is found, though not in large quantity, in the mineral kingdom, either as a saline combination, or as an ingredient in some earthy fossils. It also exists in several of the animal fluids and solids.

CHAP. III.

OF SODA.

Soda being found more extensively diffused in the mineral kingdom than either of the other alkalis, has been denominated Mineral Alkali. The term Soda is that usually applied to it, and is unexceptionable.

On the discovery of the composition of potash, Mr Davy submitted soda to the same methods of analysis, and discovered, that it is a compound of a base apparently metallic with oxygen. It required for its decomposition rather a greater degree of galvanic power than potash did; but when this was applied in sufficient intensity, the phenomena were similar; an effervescence was produced at the positive side, which was found to arise from the disengagement of oxygen gas; and at the surface in contact with the negative wire, globules were produced, having metallic lustre, these being the base of the alkali; the decomposition being effected from the powerful attractions and repulsions exerted at the different galvanic surfaces. This base, exposed to the air, absorbed oxygen, and reproduced soda; the same result took place more speedily, and with the phenomena of combustion, when it was heated in oxygen gas, thus confirming the analysis by synthesis. The quantity of oxygen in soda, Mr Davy

found reason to conclude, is rather larger than in potash, its proportion, taking the mean of various experiments, being 21.5, with 78.5 of base. To this base Mr Davy gave the name of SODIUM. The following are its principal properties:

It is white and opaque, with metallic lustre, having the general appearance of silver; it is very malleable, and is so soft, that with a slight force it can be extended in thin leaves, a softness which it retains even when cooled to 32°. Though lighter than water, its density is considerably greater than that of potassium: Mr Davy estimates its specific gravity at .9348. It requires a higher heat to melt it than potassium does: at 120 it begins to lose its cohesion; at 180 it is perfectly fused: it is also less volatile, as it remains fixed even at ignition.

When exposed to the atmosphere it is oxidated, soda being formed on its surface, which deliquesces slowly. When heated nearly to ignition, the combination is attended with combustion; the small globules of it, as they are produced in the experiment of the decomposition of the alkali, are easily inflamed by the electric spark, and when sodium is heated in oxygen gas, it burns with a vivid white light, emitting bright sparks.

From its strong attraction to oxygen, it decomposes water rapidly, soda being formed by its oxygenation, and hydrogen disengaged; and if the water is in small quantity, the heat produced is such as to inflame the sodium. It is inflamed too by nitric acid, and is rapidly oxidated by the other acids. Like potassium, it appears to be susceptible of different degrees of oxygenation; soda, when

only partially de-oxidated, forming a substance of a dark grey colour, and a similar substance being produced when sodium is fused with a portion of soda, which, when exposed to the air, or moistened, attracts oxygen, so as to pass to the perfect alkaline state.

Sodium does not appear to be dissolved by hydrogen, probably from its inferior volatility. It combines with sulphur and phosphorus, the combination being attended with the evolution of much heat and light, and the compounds being similar in external properties to those formed by potassium with the same inflammables.

It unites too with the metals, forming compounds which retain the general metallic properties. When combined with quicksilver in so small a proportion as $\frac{1}{40}$, it renders it fixed, forming a solid which has the appearance of silver. All these compounds are decomposed by exposure to air or water, the sodium by absorption of oxygen being converted into soda.

It is evident, that sodium approaches still more closely in its properties than potassium does to the common metals, as it is more dense and malleable, and less fusible and volatile; and it must be regarded as a metallic substance.

Soda is usually obtained from the combustion of marine vegetables, of which different species afford it in different quantities and states of purity. The various kinds of fuci or sea-weed, afford in this country the impure alkaline product, known by the name of Kelp; on the shores of the Mediterranean, the salsola, salicornia, and others, afford the purer barilla. Even, it, however, contains much fo-

reign matter: the soda contained in it is combined with carbonic acid, and with this are associated muriate and sulphate of soda, charcoal, lime, magnesia, and siliceous and argillaceous earths. The origin of the soda afforded by the process is not altogether determined, but it is most probable that it is ultimately derived from the muriate of soda with which these plants are from their situation supplied; as when they are transplanted to an inland situation, it is established by the experiments of Du Hamel and Cadet, that the quantity they afford diminishes progressively, and after some years they afford only potash. Vauquelin's experiments prove, that in the salsola soda, carbonate as well as muriate of soda exists previous to the combustion.

It is usually from barilla that soda is procured. The barilla in powder being lixiviated with boiling water, the solution on evaporation affords crystals of the salt formed by soda, combined with carbonic acid. To obtain from this the pure soda, it is dissolved in twice its weight of water, to which is added as much lime newly slaked as gives a thick consistence: this being poured into a glass funnel, in the neck of which a piece of linen is put, water is added as the filtration proceeds slowly, until the quantity of solution is equal to five or six times the weight of the subcarbonate that had been employed. The lime abstracts the carbonic acid, its affinity to it being aided by the large quantity of it used, and the slowness with which the solution passes through it. Still the soda has a small quantity of carbonic acid combined with it: to obtain it altogether pure, therefore, it requires to be submitted to the ac-

tion of alkohol, in the manner described under the history of potash.

Soda thus obtained is in the state of a solid white mass, which is crystallized with difficulty; its crystals are prisms, but are not regular: even in its driest state, it contains, like potash, a portion of combined water, to which it owes in part its fusibility. It is acrid and caustic, abundantly soluble in water, and is fused and volatilized by heat. It changes the vegetable colours to a green, and combines with the acids, neutralizing the acid properties: with oils it forms soap; with siliceous earth it unites by fusion and forms glass: it combines too with sulphur and phosphorus, rendering them soluble in water, and enabling them to decompose it.

So close is the resemblance in properties between potash and soda, that the distinctions between them in properties require rather minute attention to discover them. Soda appears to have a less strong attraction to water; in their combinations they can be at once distinguished, the salts formed by the one united with the acids, having qualities altogether different from those of the other. Both are applied to the same purposes.

BOOK IV.

OF EARTHS AND THEIR BASES.

THE earthy aggregates which occur in nature are usually heterogeneous or compound; but by analysing them, chemists have arrived at the knowledge of a few substances, in general insipid, of no lustre or transparency, having a loose texture, insoluble in water, uninflammable, very difficultly fusible, and of moderate specific gravity. These resisting farther analysis, they regarded as simple substances, distinguishing them still by the name of Earths, and thus affixing to this term a signification different from that which it has in popular or even in mineralogical language. Four substances of this kind were known to the older chemists, silex, argil, magnesia, and lime: other two were afterwards made known, barytes and strontites, and more lately three, zircon, glucine, and ittria, have been added to the number.

The important discovery has also been made, that they are not simple substances but compounds, their bases being somewhat similar to those of the alkalis, and these bases being united with oxygen. From the similarity of the earths in chemical properties to the metallic oxides, it had often been conjectured that they are of a metallic nature, and their reduction had frequently been attempted, and at

one time had even been supposed to have been accomplished. This, however, was a mistaken result, and nothing was truly known with regard to their composition, until Mr Davy, after his discovery of the chemical constitution of the alkalis, submitted the earths in a similar manner to the action of galvanism. Though results were obtained indicating their composition, these were much less perfect than those obtained with regard to the alkalis, owing partly perhaps to the strength of affinity between their principles, but principally to their being less perfect electrical conductors. By obviating this by submitting them to the galvanic action in mixture with potash, or with metallic oxides, results more distinct were obtained: and a method employed by Berzelius and Pontin proved still more successful,—placing them in the galvanic circuit with quicksilver. They thus obtained the metallic bases of barytes and lime in combination with the mercury. Mr Davy, by the same method, decomposed strontites and magnesia, and by distilling the quicksilver, obtained their bases. By submitting silex, argil, zircon, or glucine, to the action of the galvanic battery in fusion with potash or soda, or in contact with iron, or by fusing those earths with potassium and iron, appearances were obtained indicating their decomposition, and the production of bases of a metallic nature: and there can remain little doubt, that all the earths are compounds, and of similar constitution.

The bases of the earths obtained in these experiments approach still more nearly than the bases of the alkalis to the common metals, and the earths themselves have a stricter resemblance than the alkalis to metallic oxides.

Yet there are also grounds, as has been already stated, for retaining their distinction as a natural order, forming the link which connects the alkalis with the metals.

Of the characters assigned to the earths, none can be regarded as of itself altogether distinctive. They are usually said to be insipid; but there are three of them, barytes, strontites, and lime, which have a strong taste: they have also been considered as insoluble in water; and the greater number of them are not sensibly soluble, but still these three earths are dissolved in a certain proportion. Infusibility is a character less equivocal, as there is none of them but what requires at least a very intense heat for its fusion. They are altogether uninflammable, a property obviously arising from their being substances saturated with oxygen. In common with metallic oxides, they are destitute of metallic lustre and opacity.

The earths combine with the acids and neutralize the acid properties; these combinations, in the laws they observe, and the compounds to which they give rise, being similar to those which the alkalis form with the acids. There is an exception to this in one earth, silex, which, in the humid way, scarcely unites with any acid but the fluoric, and which does not produce the state of neutralization. It is the substance, therefore, which is at once most remote from the alkalis, and from the metallic oxides.

One property has been assigned as distinctive of the earthy from the metallic salts, that the solutions of the former are not precipitated by prussiate of potash. This is not, however, without exceptions, the earth named ittria, and also, as Klaproth has affirmed, zircon, giving

precipitates with this test. In general, the earthy salts are not much altered by infusion of galls, a re-agent which so sensibly affects metallic salts: neither are they coloured. Ittria affords also, however, an exception to this, some of its salts having a red colour, and being precipitated by infusion of galls; and from these circumstances it ought perhaps to be transferred to the class of metals, though it has not been actually reduced to the metallic state. None of these characters, indeed, is very distinctive.

Several of the earths combine with sulphur and phosphorus, and like the alkalis render these inflammables soluble in water, and capable of decomposing it. The same earths unite with sulphuretted hydrogen.

The earths and alkalis combine. By fusion with either of the fixed alkalis, they form glasses, and the alkali digested with water on several earths, dissolves a portion of them.

The earths combine with the metallic oxides by fusion, forming coloured glasses, and they even exert mutual affinities in the humid way, producing in their mixture moistened with water a degree of induration.

Lastly, the earths exert affinities to each other. Several of them combine by fusion, forming glasses more or less transparent. And when boiled together in water, it frequently happens, that an earth insoluble by itself is dissolved by the affinity exerted to it by another earth, which is itself of sparing solubility. Their mutual affinities exerted in the humid way is well displayed by another fact, that if solutions of two earths in the same solvent be mixed together, in different cases, they combine, the

power of the solvent is overcome, and they form an insoluble precipitate. And in all these combinations, the earths modify materially the properties of each other.

Of the different earths, barytes, strontites and lime have properties considerably analogous to those of the alkalis. They are to a certain extent soluble in water; their solution has an acrid taste, and changes the vegetable blue and purple colours to a green. They have hence been named Alkaline Earths, and, as has been already remarked, it has even been proposed to transfer them from the class of Earths to that of Alkalis. They are still on the whole, however, more strictly connected with the other earths; and they may be placed at the head of the order, forming the transition from the alkalis.

CHAP. I.

OF BARYTES AND ITS BASE.

THIS earth was discovered by the Swedish Chemists, Scheele and Gahn. It received the name of Terra Ponderosa, from the great specific gravity of some of its combinations, a name changed by Kirwan to that of Barytes. It occurs in nature combined with sulphuric acid and carbonic acid.

This earth had always been more peculiarly supposed to be of a metallic nature, partly from the great weight of

its native combinations, and partly from some of its saline compounds proving poisonous to animals. But this remained a mere conjecture, until the discovery of its composition by the application of galvanism. Mr Davy on placing it slightly moistened alone, or mixed with potash, in the galvanic circuit, obtained appearances of decomposition, and the evolution of metallic matter. Following the method discovered by Berzelius and Pontin, of placing the barytes in contact with quicksilver, in communication with the negative side of the galvanic battery, the analysis was more completely effected; the quicksilver had its fluidity diminished, and on exposing it to the air, it became covered with a film of barytes. And the experiment was still more successful in substituting oxide of quicksilver. He thus obtained an amalgam, from which the quicksilver was separated by distillation, leaving the metallic base of the barytes, a substance which Mr Davy named BARIUM, and which, as obtained by this experiment, he found possessed of the following properties.

It is solid, of a white colour, with metallic lustre, having a resemblance to silver. It melts at a heat inferior to ignition, but is not volatilized even when heated to redness. Exposed to the air, it tarnishes rapidly, and falls into a white powder, which is barytes, oxygen being absorbed. Dropt into water, it immediately decomposes it, evolving hydrogen, and being converted into barytes. It sinks not only in water, but in sulphuric acid, and Mr Davy supposes it to be four or five times heavier than water. It is flattened by pressure strongly applied. Mr Davy was unable to ascertain the proportion of oxygen with which

it is combined in the composition of the earth; but the facts were ascertained that it absorbs oxygen, gains weight by this absorption, and that barytes in its driest state is the product of this operation; whence it follows, that this earth is a compound of this metallic matter and oxygen.

Barytes is procured either from the native carbonate or sulphate. From the former it is obtained, as Dr Hope first shewed, by urging it with the powerful heat of a forge fire in a black lead crucible, the carbonic acid being expelled; and by dissolving the residual matter in water, the barytes may be crystallized. The sulphate may be decomposed by exposing it to a red heat for two hours in a covered crucible, mixed with one-third its weight of charcoal. By adding water to the residual matter, a compound of barytes with sulphur and sulphuretted hydrogen is dissolved; from this the barytes may be precipitated in the state of carbonate, by the addition of carbonate of potash; or by adding nitric acid, nitrate of barytes is formed, and can be obtained crystallized; and either the carbonate or nitrate thus procured can be decomposed by exposure to a sufficient heat, and the pure earth obtained.

As afforded by these processes, barytes is in the state of a grey, solid mass; its taste is extremely harsh and caustic. Exposed to the air it splits, falls to pieces, and is at length reduced to a white powder,—changes analogous to the slaking of lime, and arising like it from absorption of water.

Barytes, when combined with a portion of water, melts when raised to a red heat; when this is dissipated, it requires a more intense heat for its fusion. It appears, however, to be the most fusible of the earths.

It is soluble in water, and its solubility is greater than that of the other earths. When it has been obtained in a solid dry mass, on adding to this a larger quantity of water than is necessary to slake it, a portion of it dissolves, and afterwards forms a congeries of transparent needle-like crystals, which, according to Dr Hope, who observed this phenomenon, are flat six-sided prisms acuminated by four planes. He found them to be soluble in 17.5 of water, at the temperature of 60. The exsiccated barytes, according to Vauquelin, dissolves in 25 parts of cold water, and in twice its weight of boiling water, the latter solution forming crystals on cooling. The crystals of barytes lose their water on exposure to the air, and they suffer the same change from the application of heat. The watery solution has a strong acrid taste, and changes the vegetable blue colours to a green; a film forms on it when it is exposed to the air from absorption of carbonic acid.

Barytes combines with the acids; and as it decomposes a number of the salts which the alkalis form with the acids, it has been supposed to exert to them stronger attractions. These decompositions appear, however, rather to be owing to the exertion of the force of cohesion, from the insolubility of the compounds which it forms with these acids, than to superior strength of affinity: and in the power of neutralizing the acid properties, it is inferior

to the alkalis, and to the greater number of the other earths.

Barytes unites by fusion with the fixed alkalis, and likewise with several of the earths, though there are others of them with which it does not combine. It combines with several of them in the humid way, and communicates to them solubility, or otherwise modifies their properties. Thus it renders argil soluble in water, and silex it enables to combine with different acids.

Barytes combines with sulphur, either by fusion or by boiling them together in water, and by a resulting affinity enables the sulphur to decompose the water. It exerts a similar action on phosphorus. And it unites with some of the metallic oxides.

A chemical property which has been assigned to barytes, as distinctive of it, is that of its salts giving a precipitate with prussiate of potash, a property not belonging to the other earths, but characteristic of the metals. This precipitation, however, arises from the impurity of the prussiate, and in particular from its containing sulphuric acid. When pure, no immediate precipitation is produced by it in the barytic salt, though, after a few hours, if the solution is sufficiently concentrated, crystals of prussiate of barytes are formed.

This earth exerts considerable activity on the living system, and several of its saline combinations prove even poisonous.

CHAP. III.

OF STRONTITES.

The native carbonate of strontites, found at the mine of Strontian in Argyleshire, had been considered as a variety of carbonate of barytes, until Dr Hope shewed that the earth it contains is different from barytes and from any other. He at the same time pointed out its principal properties and chemical relations. Klaproth also and Pelletier afterwards demonstrated the existence of this as a distinct earth. It derives its name from the place where it was first found. It has besides been discovered native in different countries in the state of sulphate.

The decomposition of this earth has been effected by submitting it to the action of galvanism, in the same manner as barytes, and by a similar process its base has been obtained. To this base Mr Davy has given the name of Strontium. Its properties have been, however, only imperfectly examined. In lustre, colour, specific gravity, and other physical properties, it appeared to be similar to the metallic base of barytes; by exposure to the air it is converted into strontites, absorbing oxygen, and gaining weight in this conversion.

Strontites is obtained from either the native carbo-

nate or sulphate, by processes the same as those which have been described under the history of barytes. It is obtained crystallized, by dissolving the dry solid mass in boiling water, and allowing the solution to cool; crystals are formed an inch in length, the form of which is a thin quadrangular table, or compressed prism, sometimes bevelled at the extremities; they are transparent, but become white and opaque on exposure to the air, from losing their water of crystallization. The taste of this earth is less harsh than that of barytes, and it is not poisonous.

Crystallized strontites exposed to heat liquefies from the augmented solvent power of the water of crystallization; when this is expelled, the white powder which remains cannot be fused even by a very intense heat.

Strontites is soluble in water, the crystals requiring 50 parts at 60°; boiling water dissolves half its weight nearly. In its dry and uncrystallized state, it of course requires a much larger quantity, nearly 200 parts at 60°. The solution changes the vegetable colours to a green. This earth is likewise soluble in alkohol.

Strontites combines with the acids forming salts, of which some are soluble and crystallizable; others insoluble. The same superiority in strength of affinity has been ascribed to this earth as to barytes, from its decomposing the salts of the alkalis and other earths, but this arises from the same cause, the insolubility of the compounds it forms with the acids of the salts in which it occasions these decompositions. Its salts are in general decomposed by barytes. Dissolved in alkohol, they give

it the property of burning with a blood red flame, a property which has been assigned as one of those distinctive of this earth.

Strontites exerts no peculiar action on the alkalis, nor in general on the other earths, though with some of the latter it combines by fusion. It unites with sulphur; the compound is soluble in water, and at the same time decomposes it. On phosphorus its action is similar.

This earth resemble barytes in so many of its properties, that distinctive characters require to be pointed out, by which they may be discriminated. Strontites is less soluble in water; the forms of its crystals are different; its salts, particularly the nitrate and muriate, are considerably more soluble in water, and their solubility is augmented in a greater ratio by heat; they are decomposed by barytes; and they give a blood red colour to the flame of combustible bodies. Two re-agents distinguish them in their combinations. The watery solution of strontites is not like that of barytes precipitated by malic or gallic acid: and when the salts of strontites are decomposed by oxalic acid, the precipitate is not redissolved by an excess of acid, as that from the barytic salts is.

CHAP. III.

OF LIME.

THIS earth exists in great abundance in nature, usually in combination with acids. Its compound with carbonic acid forms the numerous varieties of marble, limestone, chalk and marl: with sulphuric acid it forms gypsum or plaster stone; and in these and other saline combinations it exists in the water of springs, in the water of the ocean, in vegetable and in animal matter.

Submitted to the action of galvanism in high intensity, lime gave indications of decomposition; and when the method described under the history of barytes was employed, Mr Davy obtained the amalgam of its base. This amalgam exposed to the air or to water, absorbed oxygen, lime being reproduced. In an experiment designed to obtain the base in an insulated state by distilling the quicksilver from it, the tube broke while warm, and at the moment that the air entered, the metal, which had the colour and lustre of silver, took fire, and burnt with an intense white light into quicklime. To this base Mr Davy gave the name of CALCIUM.

Lime is obtained with most facility from the native carbonate, from which, by a strong heat, the carbonic acid

may be expelled. This process is conducted on a large scale on the different varieties of limestone, for the purposes to which lime is applied. As it is not obtained altogether pure, the chemist, to have it in a state of purity, dissolves marble or chalk in diluted muriatic acid, leaving an excess of lime undissolved: any precipitate afforded by the addition of pure ammonia is separated; the solution is then decomposed by carbonate of potash or soda, and the carbonate of lime being washed with water and dried, is decomposed by heat.

Lime is white, moderately hard and brittle: exposed to the air it quickly absorbs water, which diminishes its cohesion, and causes it to fall down into a white powder extremely fine; this is the slaking of lime. It takes place rapidly from the affusion of water; the quantity absorbed is equal to one-fourth of the weight of the lime; and from its transition to a solid state in combining with the lime, a large quantity of caloric is evolved, producing considerable heat.

Lime is infusible; at least it does not melt in the intense heat excited by the concentration of the solar rays by the most powerful burning mirror, or that excited in the burning of combustible matter by oxygen gas.

It is soluble in water, the water at 60° dissolving about $\frac{1}{700}$th of its weight: at 212° it dissolves double that quantity, depositing the excess as it cools. The solution, Lime water as it is named, has a strong styptic taste, and changes the vegetable blue and purple colours to a green. Exposed to the air, a film forms on its surface from the absorption of carbonic acid, and the whole of the lime near-

ly is at length precipitated in the state of carbonate. The same absorption of carbonic acid takes place in dry lime, though much more slowly.

With the acids lime combines, neutralizing the acid properties. Its salts are in general decomposed by potash or soda, either of which precipitates the lime from their solutions; but not by ammonia, probably from the tendency which this alkali has to form a ternary compound with the acid and the lime.

Lime does not combine with the fixed alkalis by fusion, nor with barytes or strontites; but it unites either in the humid way, or by the application of heat, with magnesia, argil and silex.

It combines with sulphur and with phosphorus, rendering them soluble in water, and capable of decomposing it at a low temperature. It melts too, with several of the metallic oxides, forming coloured glasses; it even exerts affinities to several of them in the humid way, and in consequence of these affinities promotes the oxidation of the metals themselves by the action of air or water.

Of the different earths, lime is most extensively used. It is applied as a manure in agriculture; it forms the basis of mortar; and in practical chemistry, and many of the chemical arts, it admits of numerous applications from its chemical agencies.

CHAP. IV.

OF MAGNESIA.

THIS earth, in the state of carbonate, had been employed in medicine, and had been considered as analogous to carbonate of lime. Hoffman observed, that it formed with sulphuric acid a salt very different from that formed by lime with the same acid. And Dr Black discovering its principal properties, proved it to be essentially different from the other earths.

It is not much affected by galvanism, probably from the difficulty of rendering it a conductor of electricity. But when some of its saline compounds are submitted in the usual manner, in contact with quicksilver, to galvanic action, an amalgam is obtained, which contains the metallic base of magnesia, as this earth is formed on its surface by exposure to the air. From this amalgam, Mr Davy found it difficult to expel the whole of the quicksilver, the glass tube in which heat was applied to it being acted on. In one experiment a solid was obtained, having the white colour and the lustre of the metallic bases of the other earths, which sunk rapidly in water, producing magnesia, and was also covered with a crust of magnesia on exposure to the air. To this substance the name of MAGNESIUM may be given.

Magnesia, under various states of saline combination, exists in nature in considerable quantity. It is found, in particular, in the water of the ocean, united with sulphuric and muriatic acids, and the same salts frequently exist in mineral springs. From either of them the magnesia may be procured by decomposing them, by adding to their boiling solution an alkaline carbonate; the carbonate of magnesia is precipitated, and being thoroughly washed and dried, the carbonic acid is expelled from the magnesia by a red heat.

Magnesia obtained by this process is in the form of a white light spongy powder, very soft to the touch, inodorous, and having a slightly bitter taste. It slightly changes the blue vegetable colours to a green.

It is infusible when exposed even to the most intense heat. If previously made into a paste with water, it suffers contraction when exposed to a sudden heat.

It is insoluble in water; when dry, it absorbs a portion of water, but does not form with it a ductile paste.

Magnesia combines with the acids: its salts are in general very soluble and crystallizable, and have a very bitter taste. They are decomposed by the fixed alkalis and by the alkaline earths, the magnesia being precipitated. Their decomposition by ammonia is partial, this alkali having a tendency to form with the magnesia and acid ternary compounds.

It exerts no reciprocal action with the alkalis, nor with the alkaline earths. It combines by fusion with lime, and in the humid way it exerts an affinity to argil, combining with it, and modifying its properties.

It combines, though very imperfectly, with sulphur. By sulphuretted hydrogen it is dissolved in small quantity. On the metals or metallic oxides it exerts no evident action.

Magnesia is scarcely applied to any use, except in medicine as an antacid. Some of the native combinations of it with other earths have been used in the manufacture of porcelain.

CHAP. V.

OF ARGIL.

This earth is the base of the different clays, whence the name of Argil has been given to it. Being likewise the base of the salt, known by the name of Alum, it has received the appellation of Alumina. The former is preferable, as less ambiguous. Though it exists in nature very nearly in a state of purity, forming the sapphire and some other gems, its state of aggregation in these forms of it disguises its chemical properties; and it is therefore as it is obtained by an artificial process that it is usually described.

The decomposition of this earth by galvanism has been very imperfectly effected. The usual methods proved unsuccessful, and Mr Davy obtained only imperfect indications by another method,—submitting the argil to galvanic

action in fusion with potash or soda. The metallic matter obtained consisted principally of potassium or sodium; but with this was evidently combined a small portion of the base of the argil, for when this metallic matter was oxygenated by water, it produced not only the alkali, but a minute quantity of this earth.

The artificial process by which argillaceous earth is usually obtained, consists in dissolving common alum in water, and decomposing it by the addition of ammonia, this combining with the acid of the alum, and precipitating the argil which is its base. To this a little of the acid may however adhere; and to obtain the earth, therefore, in a state of perfect purity, the precipitate, after having been thoroughly washed, is redissolved in nitric acid, precipitated a second time by ammonia, and after being washed and dried, exposed to a red heat.

Argil, obtained by these processes, is in the state of a light white powder, spongy and soft. It is peculiarly distinguished by forming with water a paste, which, when kneaded, is tenacious and ductile; and it is from the presence of this earth that the natural clays derive their plastic quality. Though no sensible quantity of it is dissolved by water, it forms with it an imperfect combination, the loose precipitate of argil, from the decomposition of its saline compounds, being somewhat gelatinous; and if diffused in a large quantity of water, it retains a portion of it in subsiding, and even in drying, forming a kind of transparent brittle mass; while, if precipitated from a concentrated solution, without being diffused in water, it forms, when dried, a loose powder. The latter has been

named Spongy, the former Gelatinous Argil; it retains the water it has imbibed so strongly, that even exposure to a red heat does not entirely expel it.

The paste formed by kneading argil with water, contracts from the application of heat; the contraction, as has already been stated, in considering the application of this to pyrometry, continuing to proceed even at the most intense heats long after the whole of the water has been expelled. The clay at the same time acquires a great degree of hardness from its augmented aggregation. In the intense heat of the most powerful burning mirror, argil does not melt, but the fusion of it in minute quantities has been effected by the heat excited by a stream of oxygen gas directed on burning charcoal.

Argil combines with the acids, neutralizing the acid properties. Those of its salts which are soluble have a sweetish, and, at the same time, astringent taste. They are decomposed by the alkalis and alkaline earths.

Argil combines more readily than the other earths with the alkalis. When its salts are decomposed by potash or soda, an excess of either added redissolves the precipitate of argil, forming with the acid a ternary compound. They can dissolve argil alone; and they form with it by fusion a species of combination, in which the argil is rendered soluble in water.

Argil exerts affinities to the other earths, both in the humid way and by fusion. Barytes and strontites render it soluble in water. Lime forms with it an insoluble compound; but the argil in this combination renders the lime soluble to a certain extent in alkaline liquors. It also

unites in the humid way with silex, and, what is a singular effect, renders this earth soluble in acids. The combination of argil with silex by fusion, forms the basis of Pottery and Porcelain, at least these two earths form the essential ingredients, the argil communicating to the mixture that plastic quality, in consequence of which, the paste formed with water, when thoroughly kneaded, can be fashioned and turned on the lath, the silex preventing this from contracting too much in drying, and by the action exerted between it and the argil, rendering the mixture capable of that species of vitrification which forms Porcelain.

CHAP. VI.

OF SILEX.

This earth is one very extensively diffused; it forms the principal constituent part of a number of compound fossils; and those in which it predominates having usually a considerable hardness, and the silex itself being altogether insoluble in water, and in its usual state of aggregation not easily diffused, it remains when they have been disintegrated or decomposed: hence the sand of rivers and of the sea-shore is principally composed of it. Rock crystal, quartz, and flint, are fossils in which it exists almost perfectly pure, though in these its state of aggrega-

tion modifies its chemical properties, which are rather determined therefore from it in the state in which it is obtained by an artificial process.

The decomposition of silex has been very imperfectly attained. It is scarcely by itself affected by galvanic action, and when submitted to it in fusion with potash, the metallic matter obtained when exposed to the air, or dropt into water, gave indications of the regeneration of silex, so as merely to warrant the conclusion that it had been decomposed, but without affording more than imperfect results.

The process by which Silex is usually obtained, consists in fusing calcined flint with three or four times its weight of sub-carbonate of potash. The mass, when cold, is dissolved in water, and diluted sulphuric acid is added to the clear solution as long as any precipitation ensues; the precipitate is thoroughly washed with water, and dried.

Silex thus procured is in the form of a light white powder, insipid, and gritty to the touch; when mixed with water, it does not form an adhesive paste. It is extremely infusible, not melting in the intense heat excited by oxygen gas directed on burning charcoal. It melts, however, in the flame of hydrogen and oxygen gases mixed.

It is not dissolved in any appreciable quantity by water, yet there are facts which prove its solubility to a certain extent when this is not counteracted by its aggregation: if the solution of its compound with potash be decomposed by an acid, no precipitate appears, if the solution has been previously very largely diluted with water, though other-

wise it would be apparent; and it exists in solution in some mineral springs, in which no substance that can contribute to its solution can be detected.

This earth is scarcely soluble in the acids, nor does it form with any of them neutral compounds analogous to those formed by the other earths and salifiable bases, a character by which it is peculiarly distinguished. By fusion it combines with boracic and phosphoric acid, forming a species of glass; when in a state of extreme division, muriatic acid appears to dissolve a small quantity. Fluoric acid is its proper solvent, dissolving it either when the acid is gaseous, or when combined with water; though it is doubtful if the combination can be established so as to neutralize the acid.

This earth combines with the fixed alkalis. When boiled on it with water, a portion is dissolved, and by continuing the boiling, a gelatinous solution is obtained. By fusion, the combination is established perhaps more intimately, and the properties of the compound differ much according to the proportions.

When one part of flint or quartz is fused with three parts of sub-carbonate of potash, the carbonic acid is expelled, and the compound of silex and potash is partially soluble in water; with pure potash the combination is more perfect, and the compound more entirely soluble. The solution of silicated potash, or soda, becomes gelatinous when concentrated by evaporation. When kept for a number of years, crystals have been observed to be deposited from it, transparent and hard. It is decomposed by all the acids, the siliceous earth being precipitated.

With a smaller proportion of alkali the compound is less soluble, and a stronger heat is required for its vitrification: it may even be obtained altogether insoluble, transparent, and possessed of considerable hardness. Such a combination constitutes GLASS, the essential parts of which are siliceous earth, and potash or soda. The proportions are about two parts of the former, to from one to one and a half of the sub-carbonate of potash of commerce: they are intimately mixed, and the mixture is exposed to a heat sufficiently strong to expel the water and carbonic acid, and effect an imperfect combination. This is completed by afterwards applying a stronger heat, so as to produce perfect fusion, the impurities and unvitrified matter being drawn off. The glass thus formed is more transparent and colourless, as the materials have been pure. Oxide of lead is often added to communicate greater density and lustre; oxide of manganese to remove the green colour produced by iron; and by the addition of other metallic oxides in larger proportion, coloured glasses are formed.

Silex exerts affinities to the other earths, and combines with the greater number of them by fusion, forming glasses generally more or less opaque. These affinities too are frequently exerted in the humid way. Thus silex is precipitated from its solution in potash, by the attraction exerted to it by barytes, strontites, and lime.

CHAP VII.

OF ZIRCON.

The earth to which this name has been given, was discovered by Klaproth in a fossil, the Zircon or Jargon, brought as a gem from Ceylon, and it has since been discovered in the hyacinth. It is obtained from the zircon by fusing it after repeated calcinations with potash, dissolving in water, and adding to the solution muriatic acid, boiling it for a short time to precipitate more effectually the silex, with which the other earth is combined. The filtered liquor is decomposed by the addition of carbonate of soda; and the carbonate of zircon which is precipitated from it is dried, and the carbonic acid expelled by heat.

This earth, submitted to the action of galvanism in contact with potassium, affords metallic matter, which, when decomposed by water, afforded a minute portion of a powder, having all the characters of zircon.

Zircon, obtained by the above process, is a white powder, insipid, and rough. When exposed, imbedded in charcoal, to the violent heat of a forge, it undergoes a semi-vitrification; becomes so hard as to give fire with steel; has a brilliant vitreous fracture; and is of a grey colour. Its specific gravity is 4.3. When mixed with water, it imbibes it, and forms a semi-transparent jelly,

and it retains so much of this in drying, as to form a substance in appearance like gum.

It combines with the acids, and forms salts in general sparingly soluble. Those which are soluble have a sweetish astringent taste. Its affinities to the acids appear weak, as its salts are in general decomposed by a low heat, as well as by the alkalis, and all the other earths.

Zircon is insoluble in the liquid alkalis, but is dissolved by the alkaline carbonates. Its relations to the earths are scarcely known. It may be fused with silex and with argil, and a mixture of these three earths is more fusible than a mixture of two of them. It appears to combine too by fusion with some of the metallic oxides. On the inflammables it exerts no action.

CHAP. VIII.

OF GLUCINE.

THIS earth was discovered by Vauquelin, forming a constituent part of the beryl and of the emerald. Its name of Glucine is derived from the property it has of forming salts having a sweet taste. The process by which he obtained it from the beryl, was to fuse one part of it with three parts of potash; the mass, after cooling, was diffused in water, and dissolved in muriatic acid: the solution is evaporated to dryness, and, on again dissolving in water,

the silex present remains undissolved. The solution is decomposed by sub-carbonate of potash: the precipitate is digested with a solution of pure potash; the greater part of it, consisting of argil, with a portion of glucine, is dissolved; but there remains a portion undissolved, which is the glucine, sometimes coloured by oxide of iron.

Mr Davy, in attempting the decomposition of Glucine, obtained results similar to those from zircon, an amalgam being formed, when it had been placed in the galvanic circuit with mercury and potassium which decomposed water, and which reproduced glucine, when the alkali in the liquid was neutralized by an acid.

Glucine obtained pure is white, soft to the touch, and adheres a little to the tongue: it is insipid; is infusible; insoluble in water, but forms with it a paste which is somewhat ductile; this paste is not hardened by heat, nor does it contract. Its specific gravity is 2.96.

Glucine combines readily with the acids; its salts are generally soluble, and have a sweet taste.

They are decomposed by the alkalis: the earth is even completely precipitated by ammonia, which distinguishes it from argil. It is soluble in the fixed alkalis, but not in ammonia; it is dissolved, however, in carbonate of ammonia, forming a triple salt,—a property characteristic of it, though possessed also by zircon. It decomposes the salts of argil. Its relations to the other earths are not known. With borax it melts into a glass.

CHAP. IX.

OF ITTRIA.

THIS earth was discovered by Gadolin, a Swedish chemist, in a fossil found at Ytterby in Sweden, since named Gadolinite, in which it is combined with silex and lime. It has since been discovered in some other fossils. In several of its properties it resembles glucine, but it differs entirely in others.

The process followed by Vauquelin to obtain the earth from the gadolinite, was to dissolve it with the assistance of heat in diluted nitric acid, pouring off the solution from the undissolved silex. The liquor is evaporated to dryness; the residuum being dissolved in water, the compound of nitric acid and ittria is obtained: ammonia is cautiously added; and after the separation of any oxide of iron in yellow flakes, a larger quantity is added, which precipitates the earth.

Ittria is thus obtained in the form of a white powder, insipid; it is heavier than any other earth, its specific gravity being 4.842. It is not fusible alone, but with borax it forms a white glass. It is not soluble in water, but it retains that fluid with considerable force.

Ittria combines with the acids; its salts have generally a sweetish taste. Several of them too are coloured,—a

property in which it differs from the other earths. They are decomposed by the alkalis, by lime, strontites, and barytes.

Ittria is not dissolved by the liquid alkalis; nor do they redissolve it when added in excess, after having precipitated it from its solutions, which distinguishes it from glucine. It is soluble in carbonate of ammonia, but it requires a quantity five or six times greater than glucine does. Prussiate of potash throws down from its solutions a granular precipitate, of a white or pearl-grey colour. It is precipitated in grey flocculi by the infusion of galls; but very slightly by pure gallic acid. It is not affected by sulphuretted hydrogen, or hydro-sulphuret of ammonia.

The great specific gravity of this earth, its forming coloured salts, and being precipitated by the alkaline prussiates and by tannin from its solutions, in some measure connect it with the metals, and it probably ought to be regarded as a metallic oxide. It is not reduced, however, to the metallic state by heating it with charcoal, but it runs with it into a kind of semi-fluid mass, which is heavier than the earth itself. It has not been submitted to the action of galvanism.

BOOK V.

OF ACIDS AND THEIR BASES.

Acids form an order of chemical agents, distinguished by very appropriate characters, and extremely important in their chemical relations, partly from the numerous and powerful affinities they directly exert, and partly from the changes they produce in bodies by the communication of oxygen. They are compounds of inflammable bases with oxygen; and in conformity to the arrangement I have adopted, the chemical history of these bases is to be connected with the history of the individual acids.

The following are the properties characteristic of the acids. They are all sour to the taste; they change the blue, purple and red colours of vegetables to a red; they in general have a considerable affinity to water, and combine readily with it; they dissolve the metals; and they combine with the alkalis and earths, forming compounds, in which, when the due proportion is observed, the properties of the acid and of the salifiable base with which it unites are mutually lost.

The last property, that of neutralizing the properties of alkalis, is the one most eminently characteristic of acids; and these two orders of chemical agents may be considered as in their chemical relations opposed to each other,

the one always weakening the powers of the other. In combining, the acidity is diminished in proportion to the power and the quantity of alkali added: the property of alkalinity is equally weakened in proportion to the quantity and power of the acid brought into combination; and in all these cases there is a certain proportion of acid and of alkali, in which, if the combination is established, the properties of neither are apparent, but are mutually neutralized. The compound formed at this proportion, is in chemical language named a Neutral Salt. It can always be obtained in a solid state, and generally crystallized.

It has usually been supposed, that an acid and alkali have a tendency to combine more peculiarly in this proportion in which mutual neutralization is produced: and when compounds are obtained insulated, with an excess either of acid or of alkali, it has been supposed that such compounds do not arise from the immediate combination of the acid and alkali, but are formed from an affinity exerted by the neutral salt to an excess of either of its ingredients. There are no just foundations, however, for such an hypothesis. The theory connected with the most just views of the operation of chemical affinity, and most directly inferred from the phenomena, is that an acid and an alkali are disposed to combine in every proportion, each weakening the properties of the other, in proportion to the quantity of it present; and that the separation of the compound takes place at that stage of the combination where the force of cohesion is exerted with greatest strength: this will generally coincide with the point of neutralization, because there the attractive power of the

respective elements is exerted with greatest force, and the condensation is therefore greatest; but where circumstances oppose this, or give rise to a greater tendency to cohesion at another stage of the combination, the compound may become insulated with an excess of either of its ingredients. The cause most commonly productive of this, is that of one of the elements having a greater tendency to pass to the solid form than the other, this prevailing so far as frequently to produce the separation of the compound with an excess of this ingredient. In all these cases, however, whether the compound is separated in the neutral state or not, the separation of it in that state, and of course the determination of the combination in the proportions at which this happens, is the result of the operation of external forces; and the immediate effect of the mutual affinity itself is to unite the acid and alkali in all proportions. This accordingly is the result, wherever no interruption of the progress of the combination takes place from the operation of these foreign powers.

The relations of the acids to the earths is perfectly similar; they produce by their combination mutual neutralization of properties, and form compounds analogous to the alkaline neutral salts; while the combination is also not limited to this, but may be established so as to form compounds with an excess either of acid or of earth.

The different acids differ greatly in their power of neutralizing the alkalis and earths, so that to produce the state of neutralization very different quantities are required; and conversely the alkalis and earths differ as much from each other in their power of neutralizing the acids. Ac-

cording to the view delivered by Berthollet, the energy of the respective affinities of the acids to the alkalis and earths is indicated by their relative powers of producing this neutralization, the different substances being compared in the same relative weights; as the affinities of the different alkalis and earths to the acids may also be judged of from their power of neutralizing them,—the less of any of these substances, whether acid, on the one hand, or alkali or earth on the other, which is required to neutralize a given quantity of another of the opposite order, the stronger being its attraction towards it. I have, at the end of the chapter on Chemical Attraction, given the tables of Kirwan and Richter, which present the results of the experiments that have been made on the relative quantities of the different acids, and the salifiable bases that are requisite to produce reciprocal neutralization.

The action of the acids on the metals is more complicated. An acid does not directly combine with a metal; the metal must always be oxidated. Hence, if it is not previously oxidated, the first action of the acid is to communicate oxygen, either a portion of the oxygen which it contains, or a portion of the oxygen of the water present, or sometimes of the atmospheric air; and with the oxide thus formed the acid combines. The relation of the oxide is then precisely the same as that of an alkali or earth to an acid; they produce mutual neutralization of properties in the necessary proportions, and the compounds formed are perfectly analogous to neutral salts. They are named Metallic Salts.

The Neutral Salts, whether alkaline, earthy, or me-

tallic, have certain properties as an order by which they are characterized, and a common nomenclature is applied to them, which it is necessary to explain, as the history of these compounds, at least those of them formed from the alkalis and earths, is connected with that of the respective acids.

In general they are soluble in water, though they differ much in the degree of solubility: where more than 1000 parts of water are required for the solution of a salt, as the quantity dissolved is not appreciable, unless by a very accurate experiment, such salts are regarded as insoluble. The solution of salts in water is augmented by increase of temperature, this weakening the force of cohesion, which counteracts the power of attraction exerted by the water to the salt, as has been already explained. And from the various forces of cohesion in different salts, the solvent power is very unequally increased by the same augmentation of temperature.

A salt may be recovered from its solution by evaporation of the whole, or even of part of the solvent. If the evaporation has not been carried too far, so that cohesion is forcibly and irregularly exerted, producing merely aggregation of the particles, the salt is procured in a crystallized form, that is, in small masses, transparent, and of regular geometric figures, denominated Crystals. Each salt takes on a figure peculiar to it, and hence the figures of the crystals serve to distinguish them, though these are also liable to be somewhat varied by circumstances. Some salts are crystallized with difficulty; while, with

regard to others, the crystallization is easily effected, and the figures are regular. By slow or spontaneous evaporation, more regular and larger crystals are formed, than when it has been hasty. The solution which remains after a salt has crystallized, contains, of course, a portion of the same salt, which by a second evaporation may be obtained in a crystallized form.

Crystallized salts always retain a portion of water, which is essential to the crystal, the transparency and cohesion being lost when it is abstracted. The quantity is very various, and is in some cases large, amounting to more than the weight of the real salt.

From their relations to water, neutral salts derive some of their distinctive properties. Some of them liquefy, from the application of a moderate heat, owing to the solvent power of their water of crystallization being augmented; and accordingly, when this is dissipated by a continuance of the heat, a dry mass remains. This is named the Watery Fusion of Salts, and takes place principally in those which contain a large quantity of water. Some, when heated quickly, decrepitate from the sudden conversion into vapour of the small quantity of water of crystallization they contain. The crystals of many salts lose their transparency from exposure to the air, are covered with a crust, and at length fall into powder. This, which is named Efflorescence, arises from the abstraction of their water of crystallization by the air. Other salts attract water from the air, so as to become humid, and at length liquid. This property, named Deliquescence, arises from the strong attraction of these salts to water.

It remains to explain the nomenclature of the acids and of the compound salts which they form.

Acids being regarded as compounds of oxygen with certain bases, the name of each is derived from the base of which it is formed. But as this base is often capable of combining with two proportions of oxygen, and of forming two acids different from each other, these must be distinguished, and this is done by a variation in the termination of the name, the syllable *ic* being the final one, when the acid is the one which contains the larger proportion of oxygen, and *ous* where it contains the smaller proportion. Thus sulphur, by combination with oxygen in two proportions, forms two acids; the term Sulphur is the radical whence their names are derived; the one, that with the less dose of oxygen, is the Sulphurous Acid; the other, the Sulphuric. We have thus also the Phosphorous and the Phosphoric, Nitrous and Nitric, &c.

Where the base gives rise to only one acid, the name terminates in *ic*, as in the example Carbonic Acid. The acids belonging to the vegetable and animal kingdoms have a compound base, from which the name cannot be derived; it is taken, therefore, from the substance from which they are formed or prepared, as the Citric, Malic, Prussic, &c.

The nomenclature of the salts, formed by the union of the acids with the alkalis, earths, and metallic oxides, is equally systematic. All the salts formed from one acid are considered as a genus, under which are placed as species the individual salts, formed by the union of that acid with these different bases. The generic name is de-

rived, therefore, from the name of the acid; the specific name from that of the base. When the name of the acid of which the salt is composed is that which terminates in *ic*, the final syllable of the name of the salt is *at*, or rather, as Mr Chenevix has remarked, *ate*; when, again, the name of the acid terminates in *ous*, that of the salt formed from it has the last syllable *ite*. Thus, all the salts formed from sulphuric acid, constitute a genus to which the name Sulphate is applied, and the species are designated by the addition of the name of the base, as the Sulphate of Soda, Sulphate of Potash, Sulphate of Lime, Sulphate of Iron. Those, again, formed by the sulphurous acid, are named Sulphites, as the Sulphite of Ammonia, &c. On the same principle, we have Nitrates and Nitrites, Phosphates and Phosphites, Muriates, Carbonates, &c.

Salts are sometimes formed with an excess of acid or of base; and to denote these a method was proposed by Dr Pearson, which has been adopted. The genus being formed from the acid, when there is an excess of acid in a salt, the epithet *super* is prefixed to the name, when a deficiency of acid, the epithet *sub*. We thus speak of the Super-sulphate of Potash, the Sub-carbonate of Soda, &c.

Where an acid is united with two bases, as is sometimes the case, the names of both bases enter into its name,—as the Sulphate of Argil and Potash, or the Tartrate of Potash and Soda.

Acids, as has been already stated, have in the modern system of chemistry been regarded as compounds of oxygen with certain bases, and this appeared to be established by a very ample induction, resting both on analytic and synthetic chemical investigations. Without invalidating it to a certain extent, its universality has lately been rendered doubtful, and the singular proposition appears to be supported by Mr Davy's researches, that there exists an acidifying principle different from oxygen, and even superior to it in energy of action. Oxy-muriatic acid, as it has been named, a substance hitherto regarded as a compound of oxygen and muriatic acid, Mr Davy has found reason to conclude, contains no oxygen, but is a simple substance. It belongs to the same class with oxygen, in a chemical arrangement; it displays the same relation to galvanic electricity, being attracted to the positive side of a galvanic arrangement, and being therefore itself negative; and on the hypothesis, adds Mr. Davy, of the connection of chemical attraction with electrical powers, all its energies of combination correspond with those of a body supposed to be negative in a high degree. In combining with inflammable substances, it forms acid compounds: muriatic acid, for example, is a compound of it with hydrogen, and other acid products are formed by other combinations. The statement of the evidence on which these conclusions rest, belongs to the history of this substance, and of muriatic acid. It is sufficient to have given this brief view, as connected with the theory of acidity, and in considering the revolutions which chemical science at present undergoes, we can scarcely suppose that

this is the ultimate stage of the investigation. There is some improbability in the supposition of the existence of two acidifying principles, and discovery may in no long time unfold new relations amid these singular facts, and lead perhaps to a more simple theory.

If these conclusions, however, were established, they would lead perhaps to a different view of the theory of acidity. This in the present chemical system is supposed to be a property more peculiarly derived from oxygen. But it is possible that it may be a property derived rather from the bases which form acids, developed only by the combination of these bases with principles which communicate to them solubility and greater energy of chemical action, and appearing wherever the substances producing this effect are not such as neutralize acidity itself. Oxygen is the element that usually gives rise to this result; but, according to this view, it may arise from the action of others, from hydrogen for example; and the production of acidity in sulphuretted hydrogen, which has always been regarded as anomalous, may thus be accounted for. The acidifying operation of oxy-muriatic acid, if it is a simple substance, and exert such an operation, will fall to be explained from the same principle. And the singular fact, that the acid powers of oxymuriatic acid (supposing it to be a compound of muriatic acid and oxygen) are inferior to those of muriatic acid, is equally in conformity to this theory, while it is undoubtedly adverse to the hypothesis, that acidity is derived from oxygen.

CHAP. I.

OF NITRIC ACID, AND THE OTHER COMBINATIONS OF NITROGEN WITH OXYGEN.

NITRIC Acid, long known to chemists in a state of greater or less purity, is a compound of oxygen and nitrogen; and the properties of nitrogen having been already considered, the history of the acid itself, and of the other compounds which nitrogen forms with oxygen, remains to be delivered under this chapter. With a smaller proportion of oxygen than what enters into the composition of nitric acid, a compound is formed, having no acid properties, denominated therefore Nitric Oxide. With a still smaller proportion, another compound of uniform composition is produced, named Nitrous Oxide. And when nitric acid has imbibed a portion of nitric oxide, it acquires some peculiar properties, and in this state has received the distinctive appellation of Nitrous Acid.

Sect. I.—*Of Nitric Acid.*

This acid being capable of being extracted without much difficulty from a salt in which it exists, common nitre, had been long known to the chemists, and in a diluted state had been used in the chemical arts, under the name of Aquafortis. Priestley observed its partial decomposition, and its reproduction from the union of nitric oxide the product of that decomposition, with oxygen. Cavendish discovered its ultimate composition, and proved that nitrogen is its base.

This was done by a very simple experiment,—taking the electric spark for a considerable time in atmospheric air, confined in a tube. The air suffered diminution of volume, an acid was produced, and this acid was found to be the nitric. If a portion of oxygen gas were added to the atmospheric air, and the electric spark continued sufficiently long, the disappearance of the whole was nearly complete, and a similar result was obtained, from submitting to experiment a mixture of oxygen and nitrogen gases. In all these cases, the electric spark establishes the combination of the gravitating matter of the two gases, and the principal peculiarity which attends this is the slowness with which it takes place, and its not being accompanied with any sensible extrication of heat or light.

The combination is effected in other modes, in which the gases are presented in their nascent state, as in pass-

ing the vapour of ammonia over black oxide of manganese raised to a red heat.

Analysis likewise establishes the composition of nitric acid. If it be passed through an ignited glass or earthen tube, it is resolved into oxygen and nitrogen gases; its saline compounds exposed to a red heat afford the same elements; and its oxygen can be abstracted by inflammable substances, its nitrogen being evolved either pure, or retaining a portion of oxygen combined with it, which by farther operations may be abstracted.

The proportions of its principles have been variously stated. Those assigned by Cavendish were 72.2 of oxygen, with 27.8 of nitrogen; and Mr Davy has stated them not far different from these, at 70.5 oxygen, and 29.5 of nitrogen.

This acid is always obtained from the decomposition of nitre, a salt in which it exists combined with potash, and the process usually followed is that by the medium of sulphuric acid. Two parts of nitre in coarse powder are put into a retort, and rather more than one part of sulphuric acid is poured upon it, the retort being placed in a sand bath, and connected with a large receiver. A moderate heat is applied to produce distillation, and towards the end is gradually raised. The sulphuric acid combines with the potash of the nitre, and disengages the nitric acid, this decomposition being effected partly from the greater volatility of the nitric than of the sulphuric acid, and partly from the affinity of the sulphuric acid, aided by the quantity in which it is employed, this quantity being greater than that required to saturate the potash of the

nitre, and the residual mass containing therefore a considerable excess of acid. The nitric acid, however, when disengaged, is also partially decomposed; losing a little of its oxygen, a portion of it passes to the state of nitric oxide, and this being absorbed by the acid which distils over, gives it a yellow colour more or less deep, or converts it into nitrous acid. This decomposition appears to arise in a great measure from the action of the high temperature, and hence it takes place principally towards the end of the distillation.

In consequence of it, an additional process is requisite to obtain nitric acid. The coloured acid is exposed to a gentle heat, applied by a water bath; the nitric oxide holding a portion of nitric acid combined with it is expelled, and it becomes at length nearly colourless; or, what succeeds more completely, the nitrous acid is distilled from a little black oxide of manganese, which imparting to it oxygen, converts it into nitric.

Nitric acid is colourless and transparent: it emits white vapours, having a peculiar odour. Its specific gravity is from 155 to 158. It has all the acid properties, tastes sour even when much diluted, reddens the vegetable colours, and neutralizes the properties of the alkalis and others. It contains in the strongest state in which it has been obtained a quantity of water; the precise proportion is not very easily estimated, but Kirwan has inferred that in the strongest acid that can be procured, that of the specific gravity of 1.5543, at 60°, the water is equal to 26, in 100 parts.

This acid freezes by cold, the facility of congelation va-

rying considerably, according to its state of concentration: if it is highly concentrated, or if, on the other hand, it is much diluted, it freezes with more difficulty than when of intermediate strength. It is volatilized by heat, and partially decomposed, and at the temperature of ignition, the decomposition is complete, and it is resolved into oxygen and nitrogen gases. A partial decomposition of it is also effected by light; oxygen is expelled, and it passes to the state of nitrous acid.

Nitric acid has a considerable affinity to water: it attracts it from the atmosphere, and it combines with it in every proportion. In consequence of this affinity, too, it acts with energy on ice and snow, liquefying them rapidly, and thus producing intense cold.

The affinity between the elements of this acid not being powerful, it is decomposed by a number of metallic and inflammable substances which attract its oxygen partially or completely; and in consequence of this facility with which it yields oxygen, it acts with much energy on these substances.

It combines with the alkalis, earths and metallic oxides, forming salts, denominated Nitrates. These are uniformly soluble in water and crystallizable; they have a cool penetrating taste; are decomposed at a high temperature, affording oxygen, and in consequence of this deflagrate, when heated with combustible bodies.

Nitrate of Potash is the salt well known by the name of Nitre, or Saltpetre. In warm climates it is, under certain circumstances, formed spontaneously at the surface of the soil; it is thus procured in India, whence

the nitre we use is imported. In some countries of Europe, the production of it is favoured by artificial arrangements. Vegetable and animal substances, with an intermixture of old plaster, mortar, or other forms of carbonate of lime, are put into ditches lined with clay, and covered with sheds to protect them from the rain, while the air is admitted. They are turned up occasionally, and at the end of a few months, when washed with water, afford nitrates of potash and lime. A quantity of wood ashes is added to the solution, the potash of which decomposes the nitrate of lime, and increases the product of nitrate of potash; this salt is obtained in crystals by evaporation, and is purified from a portion of muriate of soda and other saline matter which adheres to it, by repeated solutions and crystallizations.

As the nitre does not pre-exist in these materials, and as indeed a fresh quantity may be obtained by exposing them again under the same circumstances to the air, it is obvious that it is formed in the process. It has been ascertained, that to the mixture of animal and vegetable matter, the addition of carbonate of lime is necessary, and the admission of the atmospheric air is indispensable. The theory of the process probably is, that the nitrogen of the animal matter combines with the oxygen of the air, and perhaps with a portion of the oxygen of the vegetable matter, and forms the acid: the carbonate of lime may favour this combination by the resulting affinity exerted by the lime, and it will attract the acid as it is formed: the vegetable matter moderates the decomposition of the animal substances, and prevents their running into that pu-

trefaction by which the nitrogen is spent in the formation of ammonia; it may farther afford the potash, which is the base of the nitre, though it has also been supposed that a part of this is formed in the process. A certain degree of humidity favours the mutual actions whence these combinations arise, and diffuses more equally through the materials the nitrous salts.

Nitre crystallizes in six-sided prisms acuminated by six planes; its taste is cool; it is soluble in seven parts of water at 60°, a production of cold attending its solution, and in an equal weight of boiling water. It melts easily: if the heat be raised, a partial decomposition of the acid takes place, and oxygen gas is expelled; and at the temperature of full ignition, the decomposition is more complete, and oxygen and nitrogen gases are disengaged.

It is from this facility of decomposition by heat that nitre produces deflagration, as has been already explained, its oxygen being communicated to any inflammable body with which it is exposed even to a moderate heat, with such rapidity that the phenomena of combustion are produced. It is from this that it is the principal ingredient in the composition of gun-powder, which consists of 75 parts of it by weight with 16 of charcoal, and 9 of sulphur. These ingredients are reduced to a state of perfect intermixture by continued trituration, a small quantity of water being added to favour this; the paste into which the composition is at length brought, is granulated by pressing it through a sieve, and the grains, after they are dry, are rounded and glazed by friction from agitation. The deflagration of the gun-powder, when an ignited spark

falls on it, is of course owing to the rapid communication of the oxygen to the sulphur and the charcoal, the sulphur in particular being easily inflamed; and its great expansive force depends on the sudden extrication of the aërial products,—sulphureous acid and carbonic acid formed by the oxygenation of the sulphur and charcoal, and nitrogen from the decomposition of the acid, probably with watery vapour, the elasticity of these being increased by the caloric rendered sensible. Another detonating composition still more powerful than gun-powder, of which nitre is the principal ingredient, is that named *Pulvis Fulminans.* It consists of three parts of nitre, two of sub-carbonate of potash, and one of sulphur triturated together: when heated, it explodes with a very loud report. Its detonation appears to be owing to the formation of sulphuret of potash, which, re-acting on the water contained in the salts, disengages sulphuretted hydrogen, and this presented in its nascent state to the oxygen of the nitre, forms sulphurous acid and watery vapour in a state of high elasticity from the caloric disengaged.

NITRATE OF SODA crystallizes in rhomboidal prisms. Its taste is cool and penetrating; it slightly attracts moisture from the air; it is soluble in three parts of water at the temperature of 60, and in an equal weight of boiling water; it is scarcely so fusible as the nitrate of potash, but is decomposed by heat in the same manner, and, like it, excites deflagration when heated with inflammable substances.

NITRATE OF AMMONIA crystallizes in slender prisms of four sides acuminated by four planes; or, if the solution

has been farther evaporated in indistinct crystals, which, when aggregated, form a compact mass, retaining less water of crystallization than the more regular crystals. Its taste is cool and bitter; it is deliquescent, and soluble in two parts of cold water, and half its weight of boiling water. Exposed to a moderate heat, it undergoes the watery fusion, and the water of crystallization is expelled; if the heat is increased, it is decomposed, and if raised to ignition, with a sudden detonation from the combination of the oxygen of the acid with the hydrogen of the ammonia. This happens at temperatures above 600: at temperatures below this, between 300 and 500, the decomposition proceeds more slowly; the products are nitrous oxide and watery vapour, and it is from this decomposition that nitrous oxide is obtained in its purest form.

Nitrate of Barytes is obtained by dissolving the native carbonate in diluted nitric acid: the solution, by evaporation, crystallizes in octaedrons, or in small brilliant plates: its taste is styptic and pungent: it is not much altered by exposure to the air: when crystallized, it is soluble in 10 or 12 parts of water at 60°, and in 3 or 4 parts of boiling water. It is decomposed by heat, its acid being converted into oxygen and nitrogen gases. It detonates, but feebly, with inflammable bodies.

Nitrate of Strontites is formed by pouring diluted nitric acid on the native carbonate. The solution, by evaporation, affords crystals, either hexaedral pyramids, or octaedrons. This salt is soluble in its own weight of water at 60°; and at 212° it dissolves in little more than half its weight. It is deliquescent in a humid atmos-

phere; in a dry atmosphere it effloresces. It is decomposed by heat, and it deflagrates feebly, when laid on burning fuel.

Nitrate of Lime is generally found in those situations in which nitrate of potash is formed. It is obtained pure by the direct combination of its principles. When the solution is evaporated to the consistence of a syrup, it affords slender prismatic crystals, deliquescent, and soluble in less than an equal weight of water at the temperature of 60, and in still less boiling water. They are also soluble in alkohol. Exposed to heat, they undergo the watery fusion, and are decomposed, the acid being expelled. By having been heated it becomes phosphorescent, and retains this property when cold. When thrown on burning fuel, it melts, and detonates slightly.

Nitrate of Magnesia has a taste bitter and acrid. Its crystallization exhibits a mass of small needle-like crystals: by spontaneous evaporation, it concretes in quadrangular prisms: it is deliquescent; is soluble in its own weight of water at 60°, and in half its weight of boiling water: it is also soluble in alkohol. By exposure to heat, it is decomposed: its acid being partly expelled, partly resolved into its constituent principles.

Nitrate of Argil.—The solution of argil in nitric acid becomes gelatinous on evaporation, and soft crystalline scales are formed. This has generally an excess of acid: its taste is sour and astringent: it is easily soluble in water, and deliquesces on exposure to the air. It is decomposed by heat. The nitrates formed from the remaining earths have been little examined, and are of no impor-

tance. The solution of ZIRCON in the acid affords a transparent resinous-like matter, not easily dried, having an astringent taste. That of GLUCINE cannot be crystallized, but by evaporation forms a gelatinous mass, which is very deliquescent. NITRATE OF ITTRIA assumes a gelatinous consistence by evaporation, and becomes brittle when this jelly cools. Its taste is sweet and astringent.

SECT. II.—*Of Nitrous Acid.*

THE name of Nitrous Acid is given to the yellow acid obtained by distillation in the usual process of decomposing nitre by sulphuric acid; and it has been remarked, that it owes its yellow colour to the presence of a portion of nitric oxide. When this is disengaged by applying a moderate heat, it becomes colourless, and if nitric oxide is transmitted through it in this state, it regains its colour, this being more or less deep, according to the quantity communicated.

Strictly speaking, therefore, there is no acid of determinate composition to which the name Nitrous can be properly applied. What is called such is nitric acid holding nitric oxide dissolved; and the quantity of this may be variable, and even indefinite, between the minimum and maximum. According to the quantity communicated, the colour is deeper. From a proportion not exceeding 1.2 of nitric oxide by weight in 100 parts, a pale yellow colour is communicated; this, as the quantity

is increased, passes through shades of bright yellow to dark orange, in which the proportion of nitric oxide amounts to about 5.5; beyond this an olive colour, and then a bright green, verging at length into blue, is obtained, and if the transmission of the nitric oxide gas be continued longer, it communicates its elasticity to the liquid acid, and the whole rises in very dense red suffocating vapours. The acid obtained by distillation from nitre and sulphuric acid is usually of a pale yellow colour: but if the heat has been raised very high towards the end of the process, it is of a deeper colour; and if any inflammable matter has been contained in the materials, it is of a dark orange red.

The colours which the acid assumes from this impregnation of nitric oxide, are likewise considerably dependent on its state with regard to dilution. If the dark orange-coloured acid be mixed with water, the different shades are produced, with a large quantity of water, blue, with more acid, olive, and bright green. These colours are not permanent; the oxygen loosely dissolved in the water, or imbibed from the atmosphere, oxygenating the nitric oxide, and bringing the whole to the state of nitric acid.

The nitric acid, by these combinations with nitric oxide, has its specific gravity diminished; a pale acid of 1.52, when converted into yellow acid, becoming nearly of the specific gravity of 1.51.

Nitrous acid in its relations to other chemical agents is similar to the nitric acid. It oxidizes in the same manner, and with the same phenomena, inflammable bodies and metals, and combines with the metallic oxides. These

combinations are indeed merely those of the nitric acid, as the nitrous oxide is disengaged during the process.

The compounds of nitrous acid with the alkalis or earths cannot be obtained by direct combination; for when it is added to any of these bases, the greater part of the nitric oxide is expelled. Some of them can however be obtained in an indirect mode, by a process pointed out by Scheele, that of exposing a nitrate, as that of potash, to such a heat as partially decomposes the nitric acid, and expels part of its oxygen. The remaining acid with a portion of nitric oxide exists in combination with the alkaline base, and these are probably to be regarded as triple compounds of these principles. They are named Nitrites. Berthollet observed that the nitrate of potash treated in this way became alkaline, so as to render green the syrup of violet, and that when an acid was poured upon it, effervescence happened, and nitrous acid vapour was disengaged. The others have not been examined very particularly, but the above characters appear to belong to all of them. On exposure to the atmosphere they absorb oxygen, and return to the state of nitrates.

As the chemical properties and agencies of the nitric and nitrous acids are so much alike, the latter is generally used in the arts, and indeed for most of the purposes to which the other might be applied, as it is more easily procured. The acid also, for the greater number of purposes for which it is used, must be diluted, and in this dilution it soon passes to the state of nitric. The *aquafortis* of commerce is a nitric acid diluted, and generally impure from the admixture of muriatic and sulphuric acids.

Sect. III.—*Of Nitric Oxide.*

During the action of diluted nitric acid on metals, a species of elastic fluid is disengaged, which was first observed by Hales, and afterwards examined by Priestley, who gave it the name of Nitrous Air, or Nitrous Gas, a name not sufficiently distinctive, as being equally applicable to another elastic fluid, and for which, therefore, that of Nitric Oxide Gas has been substituted. It is a compound of oxygen and nitrogen, containing a smaller proportion of oxygen than nitric acid. Its formation, therefore, in the above processes, is due to the metal abstracting a portion of the oxygen of the acid, the nitric oxide assuming the elastic form.

It is not always evolved pure, the abstraction of oxygen sometimes proceeding to a greater extent, and portions of nitrous oxide or nitrogen gas being evolved. It is obtained in the state of greatest purity in the action of diluted nitric acid on quicksilver or copper; one part of the concentrated acid being diluted with four or five parts of water, and poured on copper-filings in a retort; on applying a very moderate heat, the copper decomposes the acid by attracting oxygen, and nitric oxide gas is disengaged.

The relation of this elastic fluid to nitric acid is not only established by the nature of the process by which it is obtained, its composition is likewise established by its analysis. By taking the electric spark in it, it is converted in-

to nitrogen gas, and nitrous acid. When exposed to the action of substances exerting a strong attraction to oxygen, it is partially or entirely decomposed. Thus, by the action of iron or zinc, of phosphorus, or charcoal, it is converted either into nitrogen gas, the whole of its oxygen being abstracted, or into nitrous oxide, part of it only being removed. From these analytic experiments, Mr Davy fixed the proportions of the principles of this compound at 56 of oxygen, and 44 of nitrogen by weight.

Nitric oxide is permanently elastic, colourless, and therefore invisible. It is rather heavier than atmospheric air, the proportion being nearly as 100 to 92. Its specific gravity is 0.00136. 100 cubic inches of it weigh 34.3 grains.

It proves extremely deleterious to animal life. Warm-blooded animals die almost immediately on a full inspiration of it, and the irritability of the heart is destroyed. Insects which live in several other noxious gases, are quickly killed by immersion in it, and fishes die in water impregnated with it. It proves even noxious to vegetable life, the leaves of a growing plant soon becoming withered in it, and the plant dying.

Exposed to distilled water, a portion of it is absorbed equal, when the water has been previously freed from air by boiling, to 11.8 cubic inches, by 100 of water. The gas is again expelled unchanged at a temperature of 212°. By common spring water, a larger quantity is absorbed, the nitric oxide being in part converted into nitric acid, by the oxygen which water holds loosely dissolved.

When the water is impregnated with certain metallic

salts, as with the green sulphate or green muriate of iron, it condenses a much larger portion of nitric oxide gas. This has been supposed owing to a decomposition of the gas, its oxygen being attracted by the metallic salt; and in confirmation of this, it has been observed, that a portion of nitrogen exists in the residual gas. Vauquelin and Humboldt concluded, that these changes are even more complicated, one portion of the nitric oxide, according to the view they gave, attracting oxygen from the water, so as to form nitric acid, and the nitrogen of another portion of it uniting with the hydrogen of the decomposed water and forming ammonia. Mr Davy, however, has found reason to conclude from his experiments, that the gas is merely absorbed: if the action of the atmospheric air be carefully excluded, he finds that the liquid has no sensible acidity, and the nitric oxide gas may be procured from it again unchanged, either by the removal of pressure by the air-pump, or by applying a very moderate heat. It is only if the air is admitted that nitric acid and ammonia are formed. The residuum of nitrogen observed, he supposes to be merely that which had been mixed with the nitric oxide, and foreign to it; and this therefore affords a mode of determining the purity of nitric oxide gas.

Nitric oxide gas has no acid properties. Its solution in water, freed from air, does not taste sour, nor does it redden the vegetable colours. Neither does this happen from the introduction of the gas itself, previously washed in water, to vegetable coloured infusions. The colour, however, is impaired.

Nitric oxide gas is capable of supporting combustion in

some substances only, and in them only at an elevated temperature. A lighted taper immersed in it is extinguished, as is sulphur introduced in a state of inflammation. Phosphorus may be fused in it without burning; but if introduced in a state of active combustion, it burns with great splendour. Pyrophorus burns in it at a low temperature. Charcoal suspended in it in a state of ignition, burns feebly.

With oxygen nitric oxide gas combines with great facility, and this forms its most important and characteristic property. They instantly combine, and a red coloured vapour is produced, which, if the experiment be made over water, is immediately absorbed, leaving, if the gases be pure, no residuum; and what is singular in so rapid a combination of oxygen, no sensible emission of light attends the combination, and so little caloric is rendered sensible, that the vessel scarcely becomes sensibly warm to the hand. The phenomena are similar when nitric oxide gas is presented to atmospheric air; the oxygen is condensed, and if the due proportions have been observed, the nitrogen of the atmospheric air remains pure.

From the application of this combination to eudiometrical experiments, it is an object of considerable importance to determine with precision the proportions in which these gases combine so as to produce mutual condensation. But this has been found very difficult; results extremely discordant have been given on different authorities, some fixing the quantity of oxygen condensed at 100, by 200 measures of nitric oxide gases; others finding that 250, or even 300 of the latter, are condensed by 100 of the former.

These differences arise from this circumstance, that oxygen and nitric oxide are capable of combining in different proportions, or rather, that although there is one proportion in which they are mutually saturated, the compound which results from this proportion is capable of absorbing variable proportions of nitric oxide, and these are materially determined by the circumstances under which the combination takes place. The presence of water, in particular, by condensing the product, has a very important influence. If it is entirely excluded, as by combining the two gases in an exhausted globe, there is scarcely any condensation; an elastic product of a red colour is formed, and this may admit variable quantities of oxygen or of nitric oxide into the combination. But if water be admitted to condense the elastic fluid, it does so during the progress of the combination itself, determines the proportions, therefore, in which this takes place, and renders these proportions different, as it is more or less freely admitted. The larger the surface of water is over which the mixture is made, the less oxygen enters into combination with the nitric oxide, probably from the circumstance, that when a narrow surface of water is exposed to the mixture the absorption is slow, and the progress of the combination continues towards saturation, while, when the surface is large, it is absorbed as it takes place, and before the proportion in which the nitric oxide is saturated is fully established. And, on the same principle, agitation, and even the order in which the gases are presented to each other, have an influence on the results.

This property of nitrous gas of combining with oxygen gas at natural temperatures, and forming a compound quickly absorbed by water, has been applied to the purpose of eudiometry, and it has some advantages. The combination takes place so rapidly, that the result is immediately obtained, and it requires no complicated apparatus. It was introduced by Dr Priestley, and since his time has been used in different forms. It has always, however, been found very difficult to employ it, so as to obtain accurate results, owing to its being so much influenced by circumstances, which determine the combination as above explained. Hence it was nearly relinquished. Mr Dalton, however, has lately given it a preference to any other, as more expeditious, and capable of being rendered equally correct. He has observed, that nitric oxide gas may be combined with oxygen gas, so as to form either nitric acid, or nitrous acid; 36 measures of it uniting with 21 to form the former, and 72 uniting with 21 to form the latter: the combination in either proportion is determined by the manner of making the experiment; and to give accuracy to the result as a eudiometrical process, it must be conducted in such a manner as to form nitric acid or nitrous acid wholly, and without a mixture of the other. The former he has found to be most easily and most accurately effected. "In order to this, a narrow tube is necessary; one that is just wide enough to let air pass water, without requiring the tube to be agitated, is best. Let little more nitrous gas than is sufficient to form nitric acid be admitted to the oxygenous gas; let

no agitation be used, and as soon as the diminution appears to be over for a moment, let the residuary gas be transferred to another tube, and it will remain without any further diminution of oxygen. Then $\frac{7}{19}$ths of the loss will be due to oxygen." In making the experiment, therefore, on atmospheric air, add 36 measures of nitric oxide gas to 100 of air; conduct the experiment as above directed; ascertain the diminution of volume, and having multiplied this by $\frac{7}{19}$, the product indicates the proportion of oxygen which the air had contained. "The tube which Mr Dalton uses is represented Fig. 20."

Another method of applying nitric oxide gas to eudiometry was introduced by Mr Davy, that of using solutions of sulphate or muriate of iron impregnated with it, these absorbing the oxygen of atmospheric air very quickly, and producing a diminution equal to 21 in 100 parts. An apparatus for employing these solutions in eudiometrical experiments has been invented by Mr Pepys, the liquid being put into an elastic gum bottle, which is connected by a glass tube, when the experiment is to be made, with a graduated tube containing the air; by pressing the bottle, the liquid is made to act on the air with a degree of compression, which favours the result. The method is however rather complicated for common use, at least when we have others equally accurate and more simple.

Sect. IV.—*Of Nitrous Oxide.*

This, the last of the compounds of oxygen and nitrogen, was discovered by Dr Priestley, who gave it the name of Dephlogisticated Nitrous Air. Mr Davy first obtained it in a state of purity, and to him we are indebted for our knowledge of its most singular properties. He gave it the more concise appellation of Nitrous Oxide.

It is obtained by various processes, in which nitric oxide or nitric acid is partially decomposed, as by exposing nitric oxide gas to the action of iron-filings moistened with water, of iron-filings and sulphur, or of the alkaline sulphurets; and it is also disengaged in a state of mixture with nitrogen and nitric oxide during the solutions of some of the metals in nitric acid. But the process by which it is obtained most easily and in greatest purity, is in the decomposition of nitrate of ammonia by heat. This salt, in the different states of crystallization in which it exists, is decomposed, so as to afford this product at different temperatures, intermediate between 320° and 500°. Above 600° the decomposition takes place with an explosion, and the evolution of other products, principally water, nitrous acid, nitric oxide, and nitrogen gas. But this can be guarded against, by the due regulation of the heat applied by a lamp to the salt in a tubulated retort, raising it quickly to the requisite temperature, taking care not to exceed 500°, and, in particular, not to raise it so high as to pro-

duce a luminous appearance in the retort. The nitrous oxide, with watery vapour, are disengaged; the latter condenses in the neck of the retort; the former is received over water, as not much of it is immediately absorbed; it is generally white, and a little opaque, from a small portion of the nitrate of ammonia being volatilized; but this is soon absorbed by the water, and it becomes transparent.

In this process the nitric acid and the ammonia of the salt both suffer decomposition; the hydrogen of the ammonia attracts a portion of the oxygen of the acid and forms water, and the remaining oxygen is just sufficient, when combined with the nitrogen of the acid and the nitrogen of the alkali, to form this compound, nitrous oxide. Accordingly water and nitrous oxide gas are the sole products, if the temperature has not been raised too high to cause the operation of other affinities. Estimating the proportions of the elements of this compound from its formation, Mr Davy states them at 62.4 of nitrogen, and 37.6 of oxygen; and from its analysis by detonation with hydrogen, or by burning charcoal in it, he finds them to be almost the same, 63 of the one element, and 37 of the other. With this the estimation of its composition by the Dutch Chemists agrees; the proportions they give being 62.5 nitrogen, and 37.5 oxygen.

Nitrous oxide is permanently elastic. Its specific gravity is to that of atmospheric air as 161 to 100. 100 cubic inches weigh 50.1 grains. Its taste is sweetish. Its odour is very faint.

This gas is absorbed by water; the water, at a mean

temperature, and under an atmospheric pressure, takes up about half its bulk; on boiling the solution, the gas is given out unchanged; the solution has a sweetish taste, and a slight odour, not disagreeable; neither it nor the gas changes the vegetable colours. It is likewise absorbed by alkohol and by ether, communicating a sweet taste; it is again expelled by heat, and in part by the addition of water.

Nitrous oxide gas suffers no diminution of volume, nor any change of properties, when mixed with oxygen, nitrogen, or hydrogen gas. At ignition, it detonates with hydrogen. It is decomposed at a high temperature, as by transmitting the electric spark through it, or passing it through an ignited earthen tube, and is converted into nitrous acid, and oxygen and nitrogen gases.

This gas is powerful in supporting combustion. A lighted taper burns in it with an enlarged and bright flame; phosphorus with a dazzling white light; sulphur with a vivid rose-coloured flame; and iron-wire with corruscations. A higher temperature, however, is required for these combustions, than for the burning of the same bodies in oxygen gas or atmospheric air. During the combustion, a portion of nitrous acid is produced along with the product of the oxygenizement of the combustible body.

The operation of this elastic fluid on the animal system, when it is received into the lungs, is scarcely analogous to that of any other physical agent. It had been believed to be, in common with the greater number of the gases, fatal to life. Mr Davy found that it could be breathed with safety, and in his farther experiments on it, discovered

the singular effects it produces. After a few inspirations of it have been made, it causes a sense of lightness and expansion in the chest, and a pleasurable sensation begins to extend over the whole body; this increases, and is accompanied with a desire to inhale the gas; respiration therefore becomes fuller, and is performed with more energy. Exhilaration is soon produced; and if the respiration is continued sufficiently long, a crowd of indistinct ideas, often in very singular combinations, pass through the mind; there is an irresistible propensity to laughter and to muscular exertion, and violent exertions are made with alacrity and ease. These effects, after the inspiration has ceased, continue for four or five minutes, or sometimes longer; they gradually subside, and what is not the least of these singularities, the state of the system returns to its usual standard, and from this high excitement no subsequent languor or exhaustion is felt. Its operation is not however uniform on different individuals: its effects occur in various combinations; they are, as may be easily supposed, more readily excited in some than in others; and where much susceptibility has existed, alarming or unpleasant symptoms have been produced. Warm-blooded animals confined in the gas, die in a few minutes, frequently with previous symptoms of excitement; and fishes die in water impregnated with it. The gas appears during its respiration to be absorbed by the blood: this fluid acquires a purple colour, and after death the muscles are found inirritable. No satisfactory hypothesis can be advanced with regard to its operation.

Nitrous oxide can be combined with the fixed alkalis, by an indirect process discovered by Mr Davy. It consists in exposing sulphite of potash or soda, mixed with pure potash or soda, to nitric oxide gas; the sulphite attracts oxygen from the nitric oxide, and converts it into nitrous oxide, which, as it is formed, combines with the alkali, and the compound is separated by solution and crystallization from the other saline matter. These compounds, to which Mr Davy gave the name of Nitroxides, are soluble, and have a sharp taste; they cause inflammable substances to burn or deflagrate when heat is applied, and afford nitrous oxide when decomposed by the acids, or by heat.

CHAP. II.

OF SULPHURIC ACID AND ITS BASE.

Sulphur is the base of sulphuric acid. When sulphur is combined with an inferior proportion of oxygen, it forms sulphurous acid. United with hydrogen in different proportions, it forms at least two compounds, sulphuretted hydrogen and super-sulphuretted hydrogen. It farther combines with the alkalis and earths. The chemical history of all these forms the subject of the present chapter.

Sect. I.—*Of Sulphur.*

This inflammable substance exists in the mineral kingdom, both in a state of combination and in a pure form. In the latter state, it is principally a volcanic production, though native sulphur likewise occurs, which cannot be supposed to have this origin. It exists, too, in small quantity in vegetable and animal products.

Volcanic sulphur affords the greater part of the sulphur of commerce. It is usually purified by sublimation, and the sulphur is thus obtained in the form of a light powder of a yellow colour. This is easily fused, and forms a solid mass, brittle, and displaying somewhat of a crystalline, structure, and by slow cooling it may be obtained in needle-like crystals. By precipitating sulphur from its combination with an alkali by an acid, it is obtained nearly white, as it is also by dropping water on it when in fusion, or subliming it into a vessel filled with watery vapour; this whiteness has hence been ascribed to the combination of a small portion of water.

Sulphur melts at a temperature of 224°, and a phenomenon nearly peculiar to it is displayed in its fusion. If after it is fully melted, the heat be continued, or even raised, instead of flowing thinner, it becomes thick, and this thickening continues progressive, as the temperature rises even through a range of nearly 200 degrees, until it become quite viscid. The thickening, according to Dr Ir-

vine's experiments, commences at 226° of Fahrenheit, and continues to increase to 550, at which temperature the sulphur sublimes. It is quite independent of the action of the air, and does not therefore arise from oxygenation, and indeed depends on no permanent change, as by merely reducing the temperature, the liquidity is recovered, and the experiment may be repeated on the same sulphur a number of times. If poured when viscid into water, it remains for a time soft and tough, and it may be made to take the impression from a mould.

Sulphur rises in vapour, at a temperature not much higher than that at which it melts. If the air be admitted, it burns at a temperature of about 300, with a pale blue flame, and the production of pungent suffocating flames. If the heat be raised, its combustion is more vivid, as it is also in oxygen gas.

In its combustion, sulphur combines with two proportions of oxygen, forming two acids. The principal product is a gaseous acid, Sulphurous acid gas as it is named; but there is always formed with this a portion of a liquid acid not volatile, containing a larger proportion of oxygen, the sulphuric acid. The proportions of these are various, according to the circumstances of the combustion, the quantity of sulphuric acid being greater as oxygen is more freely supplied.

Sulphur combines with hydrogen, and this combination, too, appears to be established in different proportions. It unites with other inflammables, and with the greater number of the metals. It combines with the alkalis and alkaline earths, acquiring from their action so-

lubility in water, and the power of decomposing it. It also enters into combination with their metallic bases.

Sulphur had usually been regarded as a simple substance: but some facts have been more lately observed, whence it has been inferred that it contains hydrogen. Thus, the younger Berthollet found, that on passing sulphur in vapour through an ignited glass tube, traces of sulphuretted hydrogen are always obtained: and, in combining sulphur with metals by applying heat, there is an evolution of the same product: it is likewise obtained by passing the vapour of water over melted sulphur; and that in this case, it is not produced by the decomposition of the water, is proved by no portion of acid being formed. Mr Davy, in submitting sulphur to the action of galvanism, found sulphuretted hydrogen to be given out in considerable quantity; and in combining it with potassium by the application of heat, he likewise found that this product is evolved; he hence inferred, that sulphur contains hydrogen. And farther, finding reason to conclude, that oxygen exists in the composition of sulphuretted hydrogen, he supposes that this element must also be contained in sulphur. According to this view, sulphur is a compound of a base unknown, with small quantities of oxygen and hydrogen. This has scarcely been confirmed, however, by his subsequent experiments, and these results, so far at least as relates to the presence of oxygen, appear to admit of explanation on a supposition which the phenomena do not preclude, that sulphur may contain a small quantity of combined water.

SECT. II.—*Of Sulphuric Acid.*

SULPHURIC acid used to be obtained by distillation from sulphate of iron, the Green Vitriol of the older chemists, whence the name of Vitriolic Acid, by which it was known. It is now always procured from the combustion of sulphur, the method having been discovered of conducting this combustion, so that the formation of sulphurous acid is in a great measure prevented, and the principal product is sulphuric acid. The process consists in adding a small quantity of nitre,—from one-eighth to one-tenth, the weight of the sulphur. They are intimately mixed in powder, and portions of the mixture are successively kindled, and kept burning in a leaden chamber, the bottom of which is covered with water to the depth of three or four inches. The sulphuric acid, and a portion of sulphurous acid that is formed, are absorbed by the water; and when the liquor is sufficiently acid, it is removed, and by boiling it in glass retorts, the sulphurous acid and the superfluous water are expelled, and it is brought to a state of concentration, having the specific gravity of 1.842. From the nature of this process, the acid is not perfectly pure. It contains a portion of sulphate of potash, derived from its action on the potash of the nitre, and perhaps also a minute quantity of sulphate of lead. These are in a great measure precipitated by di-

luting it with water, and are more completely separated by distilling it from a glass retort.

There is considerable difficulty in determining the proportions of oxygen and sulphur in sulphuric acid, principally from the difficulty of estimating the real product of acid free from water; and hence the results of different experiments have been extremely various. The proportion of sulphur has been stated so low as 42 in 100 parts, and so high as 72. The latest experiments are those of Chenevix and Thenard: the proportions assigned from the former are 61.5 of sulphur, and 38.5 of oxygen; from the latter 55.56, and 44.44, and even these are doubtful, as the estimate of the composition of sulphate of barytes on which they rest, appears, from subsequent experiments, to be incorrect. The acid, in any state of concentration in which it can be procured insulated, has a portion of water always combined with it. At its usual specific gravity of 1.842, this is calculated by Mr Kirwan to amount to 21 in 100 parts. The greatest state of concentration in which it has been obtained is that of the specific gravity of 1.846.

Sulphuric acid of this strength is somewhat viscid, and has an oily appearance. If pure, it is colourless and transparent; it is inodorous; its taste, when it is even largely diluted with water, is intensely sour, and in very minute quantity it reddens deeply the vegetable colours. In its concentrated state, it is highly corrosive.

Sulphuric acid is congealed by cold, and even crystallizes with regularity. The temperature at which this takes place is very different, according to its concentra-

tion. When of the specific gravity of 1.843, it congeals at —15, but if it is diluted with half its weight of water, it requires a cold of —36 to congeal it. There is a certain state of dilution most favourable to the congelation; this is when the acid is at the specific gravity intermediate between 1.786, and 1.775; at this it freezes at the temperature of melting snow; if either more diluted, or more concentrated than this, the congelation requires greater cold to produce it. These facts are singular, and one not less so is, that the acid remains congealed at a higher temperature than that necessary to cause its transition to the solid form. When sulphuric acid too is impregnated with a portion of sulphurous acid, it becomes concrete even at common natural temperatures.

Sulphuric acid boils at 590°. It is decomposed at a red heat, being resolved into oxygen and sulphurous acid.

It has a strong attraction to water, so that it imbibes it from exposure to the atmosphere. It combines directly with water in every proportion, the combination being attended with a considerable increase of temperature from diminution of capacity.

It forms no combination with oxygen or nitrogen: hydrogen decomposes it at a high temperature, by attracting its oxygen; it sustains a similar decomposition from the primary inflammables; any substance, for example, containing carbonaceous matter, acts on it even in the cold; the acid becomes black from the evolution of charcoal, and a little sulphurous acid is formed. If heat be applied, the action is much more rapid, and carbonic acid and

sulphurous acid gases are disengaged with effervescence; a portion of sulphur may likewise be obtained.

The metals abstract oxygen from sulphuric acid, in general partially, so as to disengage sulphurous acid, the oxide combining with a portion of the acid that remains undecomposed. When the acid is diluted with water, it enables, by a resulting affinity, those metals which have a strong attraction to water, to attract it from the water, and hence there is a disengagement of hydrogen gas.

Sulphuric acid combines with the alkalis, earths, and metallic oxides; producing, when the due proportions are observed, mutual neutralization of properties. Its salts are named Sulphates. A considerable force of affinity is exerted between their constituent principles, and this is not much counteracted by any tendency of the acid either to elasticity or to cohesion, and hence they are not very liable to decomposition by the action of substances exerting attractions either to their acid or base. They are decomposed in general by heat: the metallic sulphates are more susceptible of this decomposition than the others, the acid being either expelled, or, by partial decomposition, giving sulphurous and oxygen gases; the earthy at a higher temperature suffer a similar decomposition. The neutral alkaline sulphates are not decomposed, with the exception of sulphate of ammonia; but when crystallized with an excess of acid, part of that excess is by heat converted into the same products. They all suffer decomposition when heated with carbonaceous matter.

Sulphate of Potash is formed by adding diluted sulphuric acid to a dilute solution of potash, or of carbonate

of potash, until the acid and alkaline properties are neutralized. A cheaper process, generally followed in pharmacy, is to prepare it from the residual mass obtained in the distillation of nitric acid from nitre and sulphuric acid, adding to it, dissolved in water, a solution of carbonate of potash, to neutralize any excess of acid, and obtaining the sulphate by evaporation. The crystals of this salt are prismatic, small and grouped; it requires for its solution seventeen parts of water at the temperature of 60°, and not more than five parts at 212°. Its taste is bitter. It is decomposed, like the other sulphates, by exposure to heat with carbonaceous matter. Acted on by nitric or muriatic acid, it suffers partial decomposition from the abstraction of part of the base, the decomposing acid acting by its affinity and quantity, and producing that participation which happens when two acids act on one base. It can combine with an excess of acid, and even with this excess crystallizes, the crystals being considerably more soluble than those of the neutral sulphate; and by the repeated action of water this excess of acid is almost entirely abstracted.

Sulphate of Soda.—This is the salt known by the name of Glauber's Salt, from Glauber the chemist, by whom its properties were first noticed. He obtained it from the residuum of the distillation of muriatic acid, from muriate of soda and sulphuric acid, this consisting of the soda of the muriate of soda, with sulphuric acid in excess. It is dissolved in water; the excess of acid is neutralized by adding lime; the fluid is allowed to remain until it becomes clear; it is drawn off into shallow leaden

vessels, and on cooling affords the neutral sulphate in crystals. It is also obtained as a residuum in other processes, particularly in the preparation of sal-ammoniac from muriate of soda and sulphate of ammonia. It crystallizes in six-sided prisms, bevelled at the extremities. Its taste is strongly saline and bitter. It is efflorescent; the crystals in a dry atmosphere soon becoming white and opaque, and at length they fall into powder. It is soluble in less than three times its weight of water at 60°, and in less than its own weight at 212°. Exposed to heat it undergoes the watery fusion; the water of crystallization is soon dissipated, and by urging it with a strong red heat it may be melted. It suffers decompositions similar to those of sulphate of potash.

Sulphate of Ammonia crystallizes in six-sided prisms acuminated by six planes, the crystals being generally slender. It is soluble in about two parts of water at 60°, and in an equal weight of boiling water; is slightly efflorescent. Exposed to heat, it melts, and is decomposed, part of the ammonia being exhaled; at ignition its acid is decomposed.

Sulphate of Barytes is formed whenever barytes is presented to sulphuric acid, in whatever state of combination either may previously exist. It is precipitated in powder, which is not soluble in water in any appreciable quantity. It is melted by a strong heat. When heated with carbonaceous matter, its acid is decomposed, and sulphuret of barytes is formed. The determination of the proportions of its constituent parts is of considerable importance, as it has been usually employed as the mode of

obtaining sulphuric acid free from water, in the experiments made to determine the proportions of the principles of that acid. The results, however, have been very discordant; but the proportions fixed by Klaproth and Withering, of 67 of earth and 33 of acid, have been lately confirmed by its analysis by Mr Thomson. Besides this neutral salt, barytes can combine with an excess of sulphuric acid; it forms a liquid that congeals into a congeries of prisms; this is decomposed, and the neutral sulphate precipitated, on the affusion of water.

Sulphate of Strontites is in the form of a white powder, insipid, and so very sparingly soluble in water, as to require, according to Dr Hope's experiments, nearly 4000 parts for its solution. It combines with an excess of acid, and is rendered more soluble in water, and crystallizable.

Sulphate of Lime, long known to chemists under the names of Gypsum and Selenite, is one of the saline substances most abundant in nature. It forms entire beds, is diffused in almost every soil, and is contained in almost all river and spring water, giving rise, when the quantity is considerable, to the quality of these named hardness. It requires about 500 times its weight of water for its solution at a mean temperature. At that of 212 it is more soluble, and this latter solution, upon cooling slowly, deposites minute crystals. Exposed to heat it appears to effervesce or boil, owing to the expulsion of its water; it becomes opaque, and falls into a white powder. This, diffused in water, speedily consolidates from a species of irregular crystallization. When exposed to a more in-

tense heat, it vitrifies if any other earth is mixed with it. Heated on charcoal, or by the blowpipe, it is partially decomposed, part of the oxygen of its acid being abstracted. Its principal use is in statuary, and in the formation of plaster or stucco work.

Sulphate of Magnesia is found in sea-water, and in many mineral waters, and is usually extracted from the brine of sea-water, Bittern as it is named, this being boiled down until it afford the sulphate of magnesia, on cooling, in acicular crystals; or sulphate of iron is added, the sulphuric acid of which combines with the magnesia of the muriate of magnesia, and increases the quantity of sulphate. Obtained in this way, it exhibits a confused mass of needle-like crystals, which are deliquescent, but this is owing to the admixture of muriate of magnesia, as the pure sulphate is rather efflorescent. By slow evaporation of its solution, it crystallizes in quadrangular prisms acuminated by four planes. These crystals are soluble in little more than their own weight of water, at the temperature of 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion at a very moderate temperature, and the dry mass which remains is melted in a strong heat, but is not decomposed. The taste of this salt is very bitter, and the bitterness of sea-water and many mineral springs is owing in part to its presence.

Sulphate of Argil, formed by dissolving the earth in sulphuric acid, crystallizes when there is no excess of acid, in scales white and of a pearly lustre, which alter little by exposure to the air: its taste is astringent: it is very soluble

in water: when exposed to heat, its water of crystallization is dissipated, and, by a stronger heat, its acid is expelled. When there is an excess of acid, the compound crystallizes with more difficulty, as, on evaporation, it assumes a gelatinous consistence. Small brilliant crystals, however, are formed in it.

The salt known by the name of Alum is a ternary compound of argil, potash and sulphuric acid; sometimes even ammonia enters into the composition, and there is always an excess of sulphuric acid; its composition, as stated by Thenard, being 26 of acid, 12.5 of argil, 10 of potash, and 51.4 of water of crystallization, frequently with a little sulphate of iron, which is to be regarded as an impurity. It is often a natural product, occurring efflorescent in the layers of what has been named Alum Slate; and it is also formed by an artificial process, from what is named Alum Ore; this, which appears to be a variety of slate, being calcined, and afterwards exposed to the atmosphere in a humid state. The saline matter is extracted by lixiviation, and when a little potash has been added, alum is obtained by crystallization. The alum of commerce is in large masses, white and transparent. When regularly crystallized, the form of the crystals is an octaedron. It is soluble in 15 parts of cold, and in two parts of boiling water: its crystals are slightly efflorescent; its taste is sweetish and astringent. Its solution reddens the vegetable colours. When exposed to a moderate heat, it melts, from the water of crystallization which it contains dissolving the solid salt; this soon evaporates, and leaves a light white powder, named Burnt or Calcined Alum. By a strong heat,

the acid is partly expelled, partly decomposed, a quantity of oxygen being afforded by its decomposition. This salt is decomposed by the alkalis, and by barytes, lime, and magnesia, which attract the greater part of the acid, and precipitate the earth with a small quantity of acid combined with it. It is also decomposed when exposed to heat with carbonaceous matter.

A decomposition of this kind, in which a large proportion of carbonaceous matter is used, affords a very peculiar product, distinguished by burning spontaneously on exposure to the air. This substance, named Pyrophorus, is prepared by exposing to heat in an iron-pot, three parts of alum, with one part of flour: the mixture liquefies, and is to be stirred constantly till the whole becomes grey, and easily reducible to powder while hot. The coarse powder is put into a coated phial, so as nearly to fill it, and this, slightly stopped with clay, being surrounded with sand in a crucible, is exposed to a red heat, until a blue flame appears at the mouth of the phial: when this has continued ten minutes, the crucible is removed from the fire, and the phial, when sufficiently cold, is accurately stopt.

This substance inflames in atmospheric air, especially in a moist atmosphere. It burns brilliantly in oxygen gas, in nitrous gas, and oxymuriatic acid gas, and is inflamed by sulphuric and nitric acids. With regard to the theory of its combustibility, it has been proved, that in order to form it the alum must contain potash; the sulphuric acid is decomposed by the carbonaceous vegetable matter, and a portion of sulphur, which is its base, is supposed to combine with the potash, and form a sulphuret,

which is intimately diffused through the argillaceous earth. There likewise remains a quantity of charcoal in the same intimate mixture, and perfectly dry. When exposed to the air, moisture is absorbed by the sulphuret, by which the temperature is raised: the sulphur is enabled, by a disposing attraction exerted by the potash, to absorb oxygen: it is inflamed, and kindles the dry carbonaceous matter, the inflammation being facilitated by their extreme division, from their intimate mixture with the argillaceous earth, and the extensive surface they thus present to the air. Mr Davy has supposed, that a portion of the potash may even be decomposed by the joint action of the sulphur and charcoal, and potassium produced, to which the combustibility may be principally owing.

Alum is used in a variety of arts. It hardens tallow: it increases the adhesive power of the farinaceous pastes; it renders water clear, which is turbid from the admixture of earthy particles; and it is one of the most essential articles in the art of dyeing, fixing the colours, and often adding to their brilliancy. It is used in medicine as a powerful astringent.

The other sulphates have been little examined. Sulphate of Zircon is insipid and insoluble. Sulphate of Glucine is difficultly crystallizable; its taste is saccharine and astringent; it is very soluble in water, its solution assuming by concentration the consistence of a syrup. Sulphate of Ittria crystallizes in small brilliant grains, of a rhomboidal form, and of a colour inclining to amethyst red. Their taste is sweet and astringent.

The remaining combinations of sulphuric acid fall to be considered under the history of the substances to which they belong. The acid itself is of extensive use. It is one of the most important agents in chemical investigations, either by the affinities it exerts, or by the oxygen it communicates. In the arts it is much employed, as in bleaching; in some of the processes of dyeing; in metallurgic operations, and in the preparation of neutral salts.

SECT. III.—*Of Sulphurous Acid.*

SULPHUROUS acid is formed in the slow combustion of sulphur, but it is mixed with a little sulphuric acid, and to obtain it pure, the process followed is to decompose sulphuric acid by the action of substances which partially abstract its oxygen, and which do not form an aëriform product. The metals produce such a decomposition, and quicksilver or tin affords the purest product. One part of either is put into a retort, with two parts of sulphuric acid; heat is applied by a lamp; the metal attracts part of the oxygen of the acid, and the sulphurous acid gas is disengaged. Being absorbed by water, it is received over mercury.

The composition of sulphurous acid has been stated at 85 sulphur and 15 oxygen. Dr Thomson, from a series of experiments on the compounds of sulphur and oxygen, gives, as the proportions, sulphur 68, oxygen 32.

This acid exists in the state of gas; but it has been reduced to the liquid state by the application of intense cold,

and strong pressure. In its usual state its specific gravity is 0.00251, or it is more than twice as heavy as atmospheric air. It has a suffocating pungent odour, proves speedily fatal to life, and instantly extinguishes combustion.

It is easily absorbed by water, 100 grains of water taking up 8.2 grains, equal to 33 times its volume. The solution has a pungent disagreeable odour, and an acid taste. It reddens some of the vegetable colours, while there are others, however, the colour of which it destroys. From the application of a moderate heat, the greater part of the gas is expelled, though the liquor remains acid, from the presence of sulphuric acid. It is singular that it is not expelled by freezing; it remains combined with the ice, and renders it so heavy that it sinks in water.

The liquid sulphurous acid slowly absorbs oxygen from the atmosphere, and is converted into sulphuric acid. If they are mixed even in the gaseous state, if a small portion of water is introduced, they gradually combine. By passing a mixture of oxygen gas and sulphurous acid gas through a tube heated to redness, sulphuric acid is also formed. Hydrogen, at the temperature of ignition, attracts its oxygen. Charcoal, at the same temperature, produces in it a similar change, and sulphur is deposited. It is not decomposed by phosphorus, and it acts feebly on the metals.

This acid combines with facility with the alkalis, forming salts denominated Sulphites, which differ considerably from the salts formed by sulphuric acid. Their taste is sulphureous; they are decomposed by a high tempera-

In its elastic state, sulphuretted hydrogen does not combine with oxygen at low temperatures; but if placed over water, their mutual action is facilitated by its medium, the oxygen combines with the hydrogen, and a thin deposite of sulphur is formed. At the temperature of ignition the combination is more rapid. If the sulphuretted hydrogen gas be kindled in contact with the atmospheric air, it burns with a blue lambent flame. When previously mixed with one or two parts of atmospheric air, it does not detonate, and the combustion of its elements is not complete, part of the sulphur being deposited on the sides of the vessel. When mixed with an equal volume of oxygen gas, and kindled, it inflames with detonation, the products being watery vapour and sulphurous acid. It is decomposed by the action of some other gases, which afford to it oxygen, as by sulphurous acid, and nitric oxide gas, the oxygen combining principally with its hydrogen, and sulphur being deposited: oxy-muriatic acid gas likewise causes a precipitation of sulphur. From the results of these decompositions, Thenard inferred, that it is composed of 70.9 of sulphur, with 29.1 of hydrogen. Mr Davy has assigned as the proportions 2.27 of hydrogen, and 32.73 of sulphur.

Sulphuretted hydrogen exerts a peculiar action on the metals. It tarnishes them quickly, or communicates shades of yellow, brown or purple, with a diminution of metallic lustre. It deepens the colour of their oxides, and if added to metallic solutions, it produces a precipitate of the metallic oxide or of the metal in combination with the sulphur, generally of a dark shade.

Sulphuretted hydrogen combines with the alkalis and earths, and displays in these combinations, powers similar to those of an acid; it neutralizes the alkaline properties, and forms compounds capable of crystallizing, and having properties analogous to those of neutral salts. And not only has it these powers; it possesses the most distinctive character of an acid in an insulated state, that of reddening the vegetable colours, at least of the colour of litmus or radish.

If this substance, therefore, be a compound of sulphur and hydrogen, it forms an exception to the universality of the proposition, that oxygen is the principle of acidity, and affords an example of an acid containing no oxygen. To obviate this conclusion, it has been supposed that oxygen may exist in its composition, and it has been remarked, that its analysis never has been executed with that accuracy which precludes this supposition, the proportions of its elements always having been inferred from experiments, in which the proportion of sulphur only was determined, and the remaining matter having been supposed to be entirely hydrogen, though for any thing that the analysis establishes it might be partly oxygen. And in all the cases of its formation, there are obvious sources whence oxygen might be abundantly supplied. This view of the constitution of this compound appeared to be established by the results of the action of potassium on it, Mr Davy having found, that when this substance is heated in sulphuretted hydrogen, previously freed from moisture by the action of muriate of lime, it burns with a brilliant flame; the gas was

changed in its qualities, being resolved principally into hydrogen; the potassium had combined principally with the sulphur, and from the products obtained by the action of muriatic acid on this compound, Mr Davy inferred that it did not consist of the potassium combined with pure combustible matter, but contained oxygen.

He has since, however, found reason to call this conclusion in question, and of course there is no direct evidence of the existence of oxygen in sulphuretted hydrogen; for the evolution of heat and light, which accompanies the action of potassium on sulphuretted hydrogen, may arise merely from the intensity of chemical action. Still there is nothing to preclude the supposition, and on the theory, that oxygen alone is the principle of acidity, analogy would be in favour of it. Or, if the other view which I have already given of the theory of acidity, (page 384), that it is a property derived from combustible bases, developed only by substances which render these bases soluble and active, it may be admitted, as remarked under the statement of that theory, that hydrogen may have this effect as well as oxygen, and that, therefore, sulphuretted hydrogen may display acid powers, though no oxygen exists in its composition.

The compounds of sulphuretted hydrogen with the alkaline or earthy bases, are formed by transmitting it in its elastic form through water, in which they are dissolved or suspended, continuing the transmission until they are saturated. They are named Hydro-sulphurets. They are soluble in water, and crystallizable; their solutions are colourless, while the air is excluded, but when it is ad-

mitted, they become turbid from decomposition; the oxygen of the air combining with the hydrogen, a portion of sulphur is deposited, and another portion, if the exposure be continued sufficiently long, combines with oxygen, forming sulphuric acid. They are decomposed by the acids, sulphuretted hydrogen being disengaged; and they precipitate of a dark colour metallic solutions.

HYDRO-SULPHURET OF POTASH, obtained by the above process, is in prismatic crystals, white and transparent; its taste is bitter and alkaline; it is inodorous when dry, but becomes fetid, if moistened. It attracts humidity from the air, is soluble both in water and alkohol, and when acted on by acids, gives out a considerable quantity of sulphuretted hydrogen.—HYDRO-SULPHURET OF SODA is also of a white colour, transparent, crystallized in tetraedral prisms, acuminated by four planes. Its taste is at first acrid and alkaline, soon becoming extremely bitter. It dissolves abundantly in water, and produces cold in dissolving: its solution is colourless, but gives a green tinge to paper: it has a smell of sulphuretted hydrogen. Acids produce with it a brisk effervescence, and render this odour very strong; but they do not render the liquid turbid. The nitrous and oxy-muriatic acids, however, produce a precipitate of sulphur.—HYDRO-SULPHURET OF AMMONIA. This compound is formed by the direct combination of its principles in their aërial form, a thin soft deposite being formed on the sides of the vessel, which exhales a penetrating vapour when exposed to the air. Another combination is obtained, by transmitting sulphuretted hydrogen through liquid ammonia, the liquid ac-

quiring a yellowish green colour, and fetid odour. Another combination long known to chemists, by the name of Fuming Liquor of Boyle, is prepared, by exposing to heat in a retort a mixture of sulphur, lime, and muriate of ammonia; a liquor distils over, of a yellow colour, which has a sharp fetid odour, and exhales white vapours. It varies considerably in the proportions of its constituent parts.

Hydro-sulphuret of Barytes is formed by transmitting sulphuretted hydrogen gas through water, in which barytes is suspended; it is abundantly soluble: and when barytes and sulphur are boiled together in water, the barytes renders soluble about one-fourth of its weight of sulphur, and a solution is formed of a yellowish red colour, which, when concentrated, deposites crystals of the form of hexaedral prisms. These according to Berthollet consist of hydro-sulphuret of barytes, without any excess of sulphur. They give out, when acted on by an acid, a large quantity of sulphuretted hydrogen. They are white, transparent, and of a silky lustre. A similar result is obtained from either of these processes with Strontites; and it is probable that the compound is of the same nature. Hydro-sulphuret of Lime can be formed by transmitting sulphuretted hydrogen gas through water in which lime is suspended. The compound is capable of crystallizing in prisms: it is soluble in water; the solution is without colour, but has a fetid smell. Sulphuretted hydrogen transmitted through water in which magnesia is suspended, dissolves a small quantity of it. Its relations to the other earths have not been examined.

II. Super-sulphuretted Hydrogen.—Besides the compound of sulphur and hydrogen, which forms sulphuretted hydrogen, they appear to combine in other proportions, so as to form different compounds. One of this kind is in particular formed by the action of alkaline sulphurets on water; it was observed by Scheele, and afterwards by Berthollet. It has been named more peculiarly Super-sulphuretted Hydrogen, and by some chemists Hydroguretted Sulphur.

If a large quantity of muriatic acid be added to a solution of an alkaline sulphuret; or if small quantities of the solution be poured into the acid, a little sulphuretted hydrogen gas is disengaged, part of the sulphur is precipitated, but a portion exists combined with the remaining sulphuretted hydrogen, forming a liquid which has the appearance of oil, of a yellow or reddish colour, and which soon subsides to the bottom of the vessel. This is what has been named Super-sulphuretted Hydrogen.

It has been little examined in its insulated state, and indeed it is not easily submitted to much chemical examination, as it is extremely susceptible of decomposition. Sulphuretted hydrogen escapes from it even at moderate temperatures, and it is also decomposed by the action of the air. In its action, however, on the alkaline and earthy bases, it forms combinations of some interest and importance.

These compounds are obtained by boiling an alkaline or earthy hydro-sulphuret with an additional proportion of sulphur. They are also formed merely by boiling sul-

phur with an earth or alkali in water, or by previously combining the sulphur with the earth or alkali by fusion, and then dissolving this in water. In either case, a decomposition of part of the water is produced; its oxygen is attracted by a portion of the sulphur and sulphuric acid formed, which is saturated by the requisite proportion of the alkaline or earthy base. The hydrogen of the decomposed water unites with the remaining sulphur, and with it and the rest of the base forms a ternary compound soluble in water; and as there is in the liquor a great excess of sulphur, the combination established is not that which constitutes sulphuretted hydrogen, but is super-sulphuretted hydrogen. It is probable even that, according to the relative proportions of the sulphur and alkali, the decomposition of the water may take place to a greater or less extent, and that these compounds may therefore vary in the proportions of their constituent principles. They are accordingly of different shades of colour, from reddish-yellow to a yellowish-green, and, what is a more direct proof of this, when they are decomposed by an acid, they afford variable quantities of sulphur by precipitation. The presence of the small portion of sulphate that is produced in their formation does not appear materially to modify their properties. They may be named, from the nature of their composition, Sulphuretted Hydro-sulphurets. The name of Hydroguretted Sulphur having been given to that compound of sulphur and hydrogen in which sulphur predominates, and this being the compound which they contain, they have been named Hydroguretted Sulphurets; but the name is so harsh that it can scarcely be adopted, and the

other, without being liable to this objection, very well expresses their constitution, and the difference between them and the hydro-sulphurets.

These liquors are transparent, of a yellow colour more or less deep, and of different tints. Their smell is slightly fetid; they appear to be liable to spontaneous decomposition from the re-action of their elements; they are immediately decomposed by the addition of an acid, which neutralizes the base, precipitates the greater part of the sulphur, and disengages the hydrogen combined with a portion of sulphur in the state of sulphuretted hydrogen. Where the alkaline liquor has been largely impregnated with sulphur, the quantity of sulphuretted hydrogen disengaged is extremely small, so that there is no sensible effervescence. The precipitated sulphur is of a pale or white colour, either from its state of aggregation or combination with water. It contains, according to Berthollet, a portion of hydrogen.

The facility with which these compounds combine with oxygen forms their most important chemical property. If exposed, either to pure oxygen or to atmospheric air, the oxygen gas is absorbed, and the liquor continues to exert this action until nearly the whole of the sulphur it contains is converted into sulphuric acid, and it becomes, of course, a solution of the sulphate of the alkali or earth with which the sulphur had been combined. This facility of combination appears to be owing partly to the sulphur being in the liquid state, whence the resistance that is opposed by its cohesion in its usual form to its combination with oxygen does not operate; and partly to the alkaline or earthy

base, by a resulting affinity promoting the combination of the sulphur and oxygen.

From this power of absorbing oxygen gas, these liquors have been applied to the purpose of eudiometry, and they afford, on the whole, one of the best eudiometers. The liquor employed has been either the sulphuretted hydro-sulphuret of potash or of lime; the latter being easily prepared in a high state of concentration, is preferred. It is obtained by boiling equal weights of lime and sulphur in 10 or 12 times their weight of water. When a tube containing atmospheric air is placed in a portion of this liquor, the oxygen of the contained air is gradually absorbed, and the liquor rises within; and if the tube has been graduated, the quantity of oxygen abstracted is indicated.

This method of operating, however, has the disadvantage of slowness; the liquor, from the smallness of the surface in contact with the air, absorbing the oxygen only very gradually, and a considerable time, too, being required to mark when the absorption has become complete. It is of importance, therefore, to accelerate the operation, and the apparatus which Dr Hope employs does so with every advantage. It consists (fig. 21.) of a small bottle designed to contain the sulphuretted solution; to the mouth of this is accurately adapted by grinding, a tube divided into 100 equal parts, and towards the bottom of the bottle is an orifice fitted with a stopper. The bottle being filled with the solution, and its orifice being covered with a flat plate of glass, it is placed under the surface of water, and the graduated tube containing the air subjected to trial, is inserted into it. The apparatus is removed

from the water, is inclined so as to allow part of the liquor to flow into the tube, and agitated strongly. It is replaced in the water, and the stopper at the under orifice withdrawn, when, from the absorption of the oxygen of the air, a quantity of water rushes in. The stopper is again introduced, the agitation renewed, and the operation is repeated until the absorption proceeds no farther. The amount of this may be determined by plunging the bottle with the tube adapted to it into water, removing the stopper of the under orifice, and taking care that the water without is at the same level as the liquor within, allowing it also to stand for a short time, that any slight rise of temperature from the application of the hand during the agitation may have ceased.

The diminution which atmospheric air suffers when subjected to this eudiometrical method, is between 21 and 22 in 100. Generally speaking, it is to be preferred to every other, as of easiest execution, and liable to fewest errors. The only fallacy to which it appears subject, is the absorption of a small quantity of nitrogen gas. If the liquor has been newly prepared by boiling, and if used without previous exposure to the air, it will, in common with any other watery liquid, absorb a portion of the atmospheric air undecomposed, or of its nitrogen as well as of its oxygen, and the substances with which it is impregnated perhaps even render the absorption of nitrogen rather greater than it would be by pure water. Accordingly, under these circumstances, it has been found that nitrogen is absorbed by these liquids; but this is easily obviated, by agitating the liquor, if it has been newly prepared, with at-

mospheric air before using it. It farther appears that when these liquors are kept for a considerable time in contact with the air, the condensed nitrogen combines with the hydrogen of the sulphuretted compound, and forms ammonia; a fresh portion of nitrogen is absorbed, and this continues to proceed, so that the diminution of volume is at length considerable; Scheele, for example, having found it to amount in atmospheric to 28 in 100 parts, undoubtedly from this cause. But, in performing the experiment in the above mode, this source of fallacy cannot operate.

The properties of the different compounds of this class with the alkalis and alkaline earths are so similar as to require no distinct enumeration. They are all liable to vary in their state of concentration from the relative quantistie of their ingredients; and there is also reason to believe, as has been already remarked, that the compound of sulphur and hydrogen which they contain, differs, from this cause, in the proportions of its constituent principles. Those of potash, soda, ammonia, barytes, strontites and lime, may be obtained highly concentrated; that with magnesia is less perfect, and contains much less sulphur dissolved.

Besides these compounds of sulphur and hydrogen, some other products have been obtained from the action of certain substances on sulphur which have been supposed to be formed of these elements. Lampadius had observed the production of a substance possessed of some singular qualities, in submitting to heat a mixture of native sulphu-

ret of iron with charcoal, coal, or bituminated wood; and the same, or a similar product, is obtained by exposing to heat a mixture of sulphur and charcoal, or passing sulphur in vapour over charcoal ignited in a tube. Lampadius, from its inflammability and volatility, named it Alkohol of Sulphur. It is liquid, colourless, or of a greenish tinge with transparency; it has a penetrating odour, is highly volatile, producing in its spontaneous evaporation a considerable degree of cold; it boils at 104, or, if the atmospheric pressure is removed, it assumes, at natural temperatures, the elastic form; it is heavier than water, its specific gravitybeing 1300; it is highly inflammable, burns with a blue flame and without smoke, and affords, by its combustion, sulphurous or sulphuric acid and a little water. It is soluble in water though sparingly, and is more abundantly soluble in alkohol. Lampadius supposed it to be a compound of sulphur and hydrogen. Clement and Desormes, on the contrary, who examined its production, consider it as a compound of charcoal and sulphur, and name it Carburetted Sulphur. The determination of this question with regard to the composition of this substance has occupied the attention of several chemists, and it does not yet appear to be altogether without doubt. Clement and Desormes observed that the charcoal disappeared in the process of its formation, if a sufficient quantity of sulphur were employed, and that in burning it gave a residuum of charcoal. The younger Berthollet, however, submitting it to examination, found that it deposites no charcoal in its combustion, and that in the products no indication of carbonic acid could be discovered; and when decomposed by oxy-

muriatic acid, there is also no trace of charcoal. Robiquet assisted by Vauquelin, obtained the same results. Hence it may be concluded, that it is a compound of sulphur and hydrogen, the hydrogen being derived, according to Berthollet, from both the sulphur and charcoal. Mr Davy has since remarked, that, from experiments made upon it, he finds it to differ considerably according to the kind of charcoal employed in its formation. If this has been imperfectly made, the product affords, by combustion, a carbonaceous residuum, while, if the charcoal had been well calcined, this could not be observed. It appears on the whole, therefore, that sulphur and hydrogen are its chief constituent principles.

In the process by which this product is obtained, other substances are formed, probably of analogous constitution, though varying in the proportions of their constituent principles. If little sulphur be employed the product is principally gaseous, has the odour of sulphuretted hydrogen, but differs from it in being less soluble in water. The liquid obtained is even of different degrees of density, according as the temperature, volatilizing more or less of the sulphur, regulates the proportions. And if there be a great excess of sulphur, a solid substance is obtained, which contains a smaller proportion of hydrogen. It has a laminated texture, a specific gravity a little inferior to that of sulphur, a fetid smell, and, when heated, gives out sulphuretted hydrogen. It is not impossible, too, but that oxygen may enter into the composition of some, or all of these products.

Sect. V.—*Of the Compounds of Sulphur with the Alkalis and Earths.*

Sulphur combines with the fixed alkalis, and with several of the earths, forming sulphurets, of which the chemical history remains to be given. These compounds are formed by exposing the alkali or earth, with the due proportion of sulphur, to a moderate heat in a covered crucible. They exist only in the solid form; for when dissolved in water new combinations are established from the decomposition of the water, as has been explained under the preceding section.

Sulphuret of Potash is formed by exposing to heat in a covered crucible, equal parts by weight of sulphur and dry concrete potash; the compound melts. When it has become concrete, it is firm and brittle, of a dark reddish-brown colour. A similar combination is obtained, by exposing to heat one part of sulphur with two parts of subcarbonate of potash, but it appears to be less intimate, part of the carbonic acid probably being retained: its colour is grey or green. Sulphuret of potash is inodorous while it remains dry; but when moistened or dissolved, acquires a fetid smell, from the production of sulphuretted hydrogen. It is fusible, and when exposed to a strong heat in close vessels, a portion of sulphur is sublimed from it. From suffering a chemical change when in a state of solution, it is scarcely possible to discover precisely its pe-

culiar agencies. One singular property belonging to it, is, that when fused with some of the metals, with gold for example, a combination is formed, which is soluble in water,—a fact observed by Stahl, and not yet fully elucidated.

Sulphuret of Soda is formed by the same process as sulphuret of potash, and has been described as similar in appearance.—Sulphuret of Ammonia does not exist, as there is no mode of bringing its elements to act on each other, without the production of sulphuretted hydrogen.—Sulphuret of Barytes is formed by exposing sulphur and barytes to a red heat in a covered crucible; the compound has a reddish-yellow colour.—Sulphuret of Strontites is formed by a similar process, as is also the Sulphuret of Lime; and in external appearance they are nearly the same.

Sulphur appears capable of combining with the bases of the alkalis and earths. Mr Davy found that it unites with potassium, when they are brought into contact in tubes filled with the vapour of naphtha; there is a rapid evolution of heat and light, and a grey substance in appearance like artificial sulphuret of iron is formed. This sulphuretted potassium easily inflames; it is also gradually oxygenated from exposure to the air, and converted into sulphate of potash. Sodium and sulphur combine with equal facility, intense heat and light being disengaged. The compound is of a deep grey colour. The phenomena displayed in these combinations are similar to those

which attend the combinations of sulphur with the metals; and the compounds have properties similar to the metallic sulphurets.

CHAP. III.

OF CARBONIC ACID, ITS BASE, AND THEIR COMBINATIONS.

In the combustion of charcoal an acid is produced which exists in the aërial form. Charcoal being a heterogeneous substance, or containing with its inflammable matter small portions of saline and earthy substances, the term Carbon was introduced to denote its pure base, and the acid formed in its combustion was hence named Carbonic Acid. Carbon, in this sense, therefore, denoted merely the inflammable matter of charcoal. But it was afterwards discovered, that the same matter exists under other forms. The diamond, which was known to be combustible, was found to yield carbonic acid as the only sensible product of its combustion, and hence came to be regarded as pure carbon. And the mineral substance known by the name of Plumbago or Graphite, was also found to be chiefly carbon with a small portion of iron. It is not certain but that charcoal, even in the purest state in which it can be prepared, contains hydrogen; and Mr Davy has supposed, that in diamond there is a small portion of oxy-

gen. The pure inflammable base, therefore, that to which the name of Carbon is appropriated, is perhaps unknown to us; and analogy, as well as the phenomena it presents in its combination with iron, might lead to the suspicion of its being metallic. The quantity of foreign matter with which it is combined in these substances, appears, however, to be small. It farther exists as a principal ingredient of all vegetable and animal substances, and is extensively distributed in the mineral kingdom: Diamond, as its purest form, may first be considered.

SECT. I.—*Of Diamond.*

THE Diamond, the gem which, from its lustre and hardness, is of greatest value, is found in India and in Brazil. It occurs crystallized, is colourless or tinged of various shades, transparent, and has a laminated structure; in hardness it is superior to every other substance; its specific gravity is 3.5.

From its high refractive power, Newton conjectured that the diamond must be an inflammable body. It was found to be dissipated when placed in the focus of a powerful burning mirror, and even in the heat excited in a furnace. In the latter mode of making the experiment, its surface was observed to be luminous; and at length it was ascertained, that at a temperature sufficiently elevated it suffers a real combustion. The object of inquiry was then to ascertain what is the product of its combustion; La-

voisier, making experiments with this view, observed, that if the diamond were not highly heated, its surface became covered with a thin coating of charcoal, and when by raising the heat higher the combustion was rendered complete, the only sensible product was carbonic acid. He concluded, therefore, that there exists a great analogy between diamond and charcoal in chemical constitution.

Mr Tennant, some years afterwards, burning the diamond by the aid of nitre in a gold tube, concluded from the product of carbonic acid, that the quantity afforded by a given weight of diamond is the same as is afforded by the same weight of charcoal, and hence inferred, that the diamond differs from charcoal only in the state of aggregation and its crystallized form. Guyton, from a series of experiments, advanced a different opinion. Placing the diamond in pure oxygen gas, and heating it by directing on its surface the solar rays concentrated by a lens, he observed, as Lavoisier had before done, that its surface was first charred; when the heat was applied in more intensity this disappeared, and it began to burn with a glow of light. On estimating, at the end of the experiment, the quantity of carbonic acid it produced, it exceeded considerably the quantity that would have been produced from the consumption of the same weight of charcoal, 100 parts of carbonic acid, as he stated the results, being obtained from the disappearance by combustion of 17.88 of diamond, while the same quantity only is formed from the combustion of 28 of charcoal. He concluded, therefore, that the difference between these two substances is, that

the diamond is the pure carbonaceous base, while charcoal is an oxide of carbon.

The mode, however, in which Guyton estimated the quantity of carbonic acid was not free from objections, and more lately Messrs Allen and Pepys have repeated the experiment of the combustion of these substances in oxygen gas, and have found that the proportions of oxygen consumed, and of carbonic acid formed from equal weights of each are the same; whence they have concluded, as Mr Tennant had before done, that they differ merely in aggregation and form. I shall have to state that there is some reason to conclude, that charcoal contains a small quantity of hydrogen, and Mr Davy has supposed, that diamond may contain a minute quantity of oxygen. These differences may exist without being capable of being discovered by any difference in the products of combustion, as the small portion of hydrogen in charcoal will form water, which will be retained in combination with the carbonic acid gas.

The diamond requires a high temperature to cause it to burn, and, even when kindled in oxygen gas, does not evolve so much caloric as to support the necessary heat. It presents different appearances, according to the temperature; its surface being blackened if the heat is not sufficiently high, and the illumination being brighter as it is raised.

The diamond is scarcely acted on by any other agent. By sulphuric acid heated on it, it appears to be charred; the other acids do not affect it, an inertness evidently owing to its state of aggregation.

Sect. II.—*Of Plumbago, &c.*

This substance, the Black Lead of Commerce, is a mineral production. Its relation to carbonaceous matter, and at the same time the existence of iron in it, were first observed by Scheele; and from subsequent experiments by Pelletier and Monge, it was inferred to be a compound of carbon and iron, containing from 5 to 10 of iron in 100 parts. Guyton supposed, that it consumes more oxygen in its combustion than charcoal, and that, therefore, though an oxide of carbon, it approached nearer to the pure inflammable base. This conclusion rested on no decisive evidence; and Messrs Allen and Pepys have found, that the carbonaceous matter of it consumes the same quantity of oxygen, and affords the same quantity of carbonic acid as charcoal. Mr Davy regards it as carbon combined with iron, and has supposed, that as it exists in this combination, the carbon approaches to the metallic state, the compound being a conductor of electricity, opaque, with considerable lustre. It so far approaches in chemical characters to the diamond as to be little acted on by any chemical agent, and to be so imperfectly combustible as to require a very elevated temperature, and the continued application of external heat to cause it to burn.

The substance named Mineral Carbon, Incombustible Coal, or Anthracite, appears, so far as regards its carbonaceous matter, to be in a similar state. It differs from other

coals in containing no bitumen; and it is much less combustible, burning only at an elevated temperature, and scarcely evolving so much heat as is sufficient to sustain its combustion. With carbonaceous matter it contains portions of silex, argil, and iron. Guyton had supposed it to be an oxide of carbon at a lower degree of oxidation than common charcoal; but Allen and Pepys have found that it consumes in burning the same quantity of oxygen, and affords the same quantity of carbonic acid; and its inferior combustibility is probably owing to its state of aggregation.

SECT. III.—*Of Charcoal.*

CHARCOAL is obtained from the imperfect combustion of wood; the wood cut into billets being reared in a pile which is covered with earth or turf, apertures being left to regulate the circulation of air, by which the combustion, when the wood is kindled, is supported. This combustion is carried on as slowly as possible; the volatile principles of the wood, particularly its oxygen and hydrogen, with a portion of its carbon, form volatile products, which are disengaged; and there remains at length the black porous substance which forms common charcoal, retaining frequently the figure and texture of the wood. To prepare it thoroughly, it requires to be exposed to a red heat with the exclusion of the air: this is done by covering it with sand. By the same method, well prepared charcoal may at

once be obtained from wood, a heat sufficiently intense having been applied.

From the nature of this process, it is obvious that there must exist in the charcoal any other matter not volatile which entered into the composition of the wood; and accordingly it always contains portions of saline and earthy matter, chiefly carbonates of potash and lime, with a little oxide of iron. But these are present in comparatively minute quantities, and do not appear to modify its properties. Apart from these charcoal was regarded in the modern system of chemistry as pure carbon. Guyton, however, as has been already stated, supposed it to be an oxide of carbon; while Allen and Pepys, finding that it consumes the same quantity of oxygen, and forms the same quantity of carbonic acid, established again the former opinion.

There are some facts, however, which still render this doubtful, and which are favourable to a conclusion advanced by Berthollet, that charcoal contains hydrogen. In particular, when charcoal is burnt in oxygen gas a sensible quantity of water is deposited; when it is urged with a strong red heat, a quantity of elastic fluid is given out, composed of carbon and hydrogen; and when heated with sulphur, in the experiments already referred to, sulphuretted hydrogen, or super-sulphuretted hydrogen is disengaged.

It is true, that there are some sources of fallacy, whence it might be supposed that these results arise. If charcoal is not thoroughly calcined, a portion of the hydrogen of the vegetable matter may exist in it, which however may

not be essential to it, and may be expelled if the charcoal is more completely prepared. It appears too, that charcoal imbibes humidity very rapidly, absorbing it even from the air, and in such experiments this may be the source of the hydrogen which appears.

The operation of both these causes is unquestionable in some of the experiments which have been made on this subject, but there are others in which we can scarcely admit their influence, and in which the existence of hydrogen in charcoal is still indicated. In particular, when charcoal has been thoroughly calcined by exposure to an intense heat, and immediately on its removal from the fire, without being allowed to cool under exposure to the air, is mixed with sulphur, the mixture, when urged by heat, affords both sulphuretted and super-sulphuretted hydrogen, and in such quantities, that the hydrogen existing in these products cannot be supposed to be derived from the sulphur alone. Mr Davy also finding that a small quantity of aërial fluid is given out in submitting charcoal in the best state of preparation to the intense heat of a galvanic battery, has supposed that it contains a minute proportion of hydrogen.

There are even some facts from which the existence of a little oxygen in charcoal may be inferred, particularly the singular one observed both by Lavoisier and Guyton, that the diamond, when heated in oxygen gas, is charred on its surface. And theory would lead us to conclude, that minute portions both of oxygen and hydrogen may exist in it, for being obtained from products in which these elements exist, and from which they are expelled by heat, in

proportion as their expulsion proceeds, the affinity of the carbon to the remaining portions must become stronger from the increase in its relative quantity; and minute quantities may, and probably will be retained with a force, which even a very intense heat will be unable to overcome. The only difficulty in this view of the subject arises from the fact apparently established, that the same quantity of carbonic acid is produced in burning from charcoal as from diamond, and the same quantity of oxygen consumed. But if the quantity of hydrogen is small, the water which it will form may exist in the elastic form combined with the carbonic acid, and add so far to its volume, as that this shall appear equal to the volume of carbonic acid produced from the combustion of the same weight of diamond, though this contain no hydrogen. And as hydrogen combines with rather a larger proportion of oxygen than carbon does, this may even give rise to the apparent equality in the consumption of charcoal and diamond, though the former contain even a small quantity of oxygen as well as of hydrogen.

From all these considerations, it must appear doubtful, if the pure carbonaceous base is still known to us in its insulated form. And the observation by Mr Davy is very just, that minute differences in chemical composition may produce great differences in external and physical characters.

Charcoal well prepared is brittle and porous, tasteless and inodorous; it is also procured by some processes in the state of a powder. It is infusible in any heat that a furnace can raise; but by the intense heat of a very power-

ful galvanic apparatus, it is hardened, and at length is both fused and volatilized. In its common state it gives out, when exposed in close vessels to a heat above redness, an elastic fluid, consisting principally of a variety of carburetted hydrogen: this diminishes as the heat is raised, and at length the production of it ceases. But even when it has been brought to this state, a small portion of gas is expelled by the more intense heat which galvanism excites. This evolution of aëriform matter is to be ascribed, in the earlier stages of the process, probably principally to the decomposition of water which the charcoal had imbibed, and accordingly part of it is always carbonic acid: the smaller quantity evolved at more intense heats is probably derived from the minute portion of hydrogen and perhaps of oxygen combined with the carbonaceous base. By this high degree of calcination the charcoal is rendered a better electrical conductor.

Charcoal is insoluble in water, and is not affected by it, nor does it at low temperatures produce on the water any change. It absorbs a small portion of it, and hence, in cooling, it imbibes it from the atmosphere so as sensibly to increase in weight. At the temperature of ignition it decomposes water, the products being carbonic acid gas and a variety of carburetted hydrogen gas.

A very singular property belonging to charcoal, is that of absorbing the different aërial fluids in considerable quantity without forming with them any intimate combination. If the charcoal, when ignited, is allowed to cool without exposure to the atmosphere, on exposing to it any gas the absorption takes place, and exceeds many times

the volume of the charcoal. The extent of it is different with different aërial fluids: carbonic acid, muriatic acid, and ammonia, are largely absorbed, while oxygen, nitrogen, and hydrogen, are absorbed more sparingly. The condensed gas appears to suffer no chemical change; and the greater part of it is again expelled by a heat inferior to that of boiling water, and also to a certain extent by immersion in water. Neither is there any apparent alteration in the properties of the charcoal. It is therefore a mere mechanical condensation, produced, probably, however, by a certain attraction exerted by the carbonaceous matter to the aërial fluid. Two gases thus condensed in the pores of the charcoal have been found to combine; oxygen and hydrogen when absorbed together, for example, forming water, and this being accompanied with a sensible elevation of temperature.

When the action of oxygen and of hydrogen gases is favoured by humidity, they appear to dissolve small portions of charcoal at common temperatures. At the temperature of ignition they form with it intimate combinations. In burning, charcoal combines with oxygen gas, forming carbonic acid. And if hydrogen gas be passed over charcoal in an ignited tube, an elastic fluid formed from their combination is obtained. Nitrogen does not unite with it. It appears to form combinations with sulphur, either alone or with hydrogen, some of the products from the mutual action of sulphur and charcoal at high temperatures being compounds of this kind, as has been already noticed.

The alkalis scarcely sensibly dissolve charcoal when it is

pure, though in its common state they receive from it a dark brown colour. It decomposes a number of the acids by abstracting their oxygen, some suffering this decomposition at a low, others only at a high temperature.

One very singular property, undoubtedly chemical, belonging to charcoal, remains to be stated: it is that of removing the odour, taste, and colour of a number of vegetable and animal substances, when triturated or digested with them by the medium of water. Thus, all saline substances, which, from the adherence of vegetable or animal extractive matter, are of a brown colour, may, after this process, be obtained white by a second crystallization: carbonate of ammonia, which is fetid and dark coloured when obtained from the decomposition of animal matter by heat, is rendered perfectly white and pure by sublimation from charcoal powder. Resins, gum-resins, balsams, and essential oils, even those that have the strongest smell, are rendered nearly inodorous when they are rubbed with charcoal and water, or when solutions of them in alkohol are macerated with the charcoal, or filtrated repeatedly through it; and a number of the vegetable tinctures and infusions lose their colour, smell, and much of their taste, by the same process. It is from this agency that charcoal powder removes the offensive smell and taste which water acquires from keeping in wooden casks, and that it obviates even the putrescence of animal matter. To produce these effects, it is necessary that the charcoal should have been well calcined and newly prepared, or at least should have been long exposed to the air. A certain quantity too is necessary, more or less, according to the

effect required. It is not very obvious by what kind of agency the charcoal produces these effects.

Sect. IV.—*Of Carbonic Acid.*

This is the Fixed Air of Dr Black, the first of the aëriform fluids which was submitted to accurate examination. He investigated a number of its properties, and the changes it produces in chemical combinations, particularly with the alkalis and earths. Bewly and Bergman discovered its acid powers, which, from being comparatively weak, had escaped Dr Black's observation.

Though this acid is produced without difficulty by the direct combination of its constituent principles, it is usually obtained by other processes. It exists, combined with lime, in the different varieties of limestone, marble, and chalk; and if any of these be exposed to a strong red heat, the affinity of the acid to the lime is so far weakened, that it assumes the elastic form. Or, if the affinity of another acid to the lime is introduced, the same result is obtained without applying heat. If into a bottle fitted with a bent tube, small fragments of chalk or marble are put, and if to this diluted sulphuric or muriatic acid is added, a strong effervescence is immediately excited from the disengagement of the carbonic acid gas, the sulphuric or muriatic acid combining with the lime: the gas may be collected over water, by which it is not immediately absorbed in any considerable quantity.

The experiment of the formation of this acid, however, by the direct combination of its principles, is of importance, as determining its composition with regard to their proportions. Lavoisier, in performing this experiment by burning charcoal in oxygen gas, the charcoal having been previously thoroughly ignited to avoid as much as possible any error from the production of water, which is always observed when this precaution is not taken, fixed the proportions of the principles of the acid at a mean at 28 of charcoal and 72 of oxygen; and with this the results of the experiments of Clement and Desormes, and more lately of Messrs Allen and Pepys, almost exactly agree, the proportions assigned by the latter chemists being 28.6 of carbon and 71.4 of oxygen. It is not perfectly certain, as has been already remarked under the history of charcoal, but that a little water may be formed, from the small portion of hydrogen which that inflammable substance probably contains, and may exist in the carbonic acid gas; but the quantity, if it do exist, must be regarded as very minute. It appeared, from some of these experiments, that in this formation of carbonic acid gas there is a sensible condensation; but this appears to have arisen from the operation of other circumstances: and in those performed by Allen and Pepys it was not observed, the oxygen gas combining merely with charcoal to form carbonic acid, by which its density was altered, but its volume not changed.

The composition of carbonic acid has been established by its analysis. This is effected by a concurrence of affinities: a few pieces of phosphorus are put at the bottom

of a coated glass tube, and over this is put a quantity of marble (carbonate of lime) in powder, or what renders the experiment more easy of execution, carbonate of potash or soda dried. The part of the tube containing the carbonate is placed across a small furnace, so as to be brought to a red heat: the heat communicated to its extremity is sufficient to volatilize the phosphorus, and this passing over the ignited carbonate, decomposes the carbonic acid, by attracting its oxygen: phosphoric acid is thus formed, which unites with the base of the carbonate, and the carbonaceous base of the acid remains diffused through the mass in the state of charcoal perfectly black. It may be collected by dissolving the saline matter, and when dried has all the properties of common charcoal. The decomposition is probably produced by the joint affinities of the phosphorus, and the alkaline or earthy base with which the carbonic acid is united to its oxygen, aided by the state of condensation of the acid, or to its being acted on in a nascent state as disengaged by the heat. Potassium, from the strength of its affinity to oxygen, decomposes carbonic acid with facility, burning in the gas, and precipitating charcoal. And a partial abstraction of its oxygen is even effected by some of the metals, as iron or zinc, at a high temperature.

Carbonic acid has a greater specific gravity than the other elastic fluids: it is compared with atmospheric air as 0.0018 to 0.0012, or is one half heavier; it is inodorous, has a pungent taste; it proves eminently fatal to life, an animal immersed in it being immediately killed, and even

when diluted with two or three parts of atmospheric air, it exerts a deleterious power.

Carbonic acid in its elastic form is absorbed by water, the water, at a mean atmospheric pressure and temperature, absorbing nearly its own volume. The absorption is promoted by agitation, and the quantity absorbed is increased by cold, or by augmented pressure. The water, when largely impregnated with it, sparkles when shaken, and has a pungent taste; the gas escapes on exposure to the atmosphere: it is entirely expelled by boiling, and is disengaged by freezing.

The acidity of carbonic acid is weak, and tests of some delicacy are required to discover it. Its taste is scarcely perceptibly sour, either in its elastic or liquid form; it reddens, however, the more delicate vegetable colours, as that of litmus; and though it adheres with little force to the bases with which it combines, this Berthollet ascribes to its greater tendency to pass into the elastic state; and judging from its powers of saturation, it may even be regarded as superior in acidity to a number of the other acids.

It combines with the alkalis, earths, and metallic oxides, forming salts denominated Carbonates. In these combinations, at least with the alkalis, is displayed the peculiarity, that the alkaline properties are rather impaired than neutralized; it is at least difficult to establish neutralization, and the compounds, even when obtained of uniform composition by crystallization, retain to a certain extent the alkaline properties; they have the alkaline taste, change to a green the vegetable colours, and combine with oils so as to form soaps. The alkalis in this state were there-

fore formerly regarded not as compounds; they were supposed to be in their purest form, were named Mild Alkalis, to distinguish them from what were named Caustic Alkalis, which were supposed to be less pure. Dr Black shewed, that the mild state, as it was named, is owing to the presence of carbonic acid; and Bergman proved, that in this state they are to be regarded as compound salts. They generally form, however, with an excess of base, and it is not very certain if they can be obtained otherwise, at least in a crystallized state. The property by which they are peculiarly distinguished, is that of effervescing strongly on the addition of any acid, the carbonic acid being disengaged, and assuming the elastic form. They are also easily decomposed, at least partially, by heat, the carbonic acid being expelled. In the earthy carbonates, however, it is retained with more force, and requires a much higher heat.

Sub-carbonate of Potash.—It is under the form of this salt that potash is afforded in the processes by which it is usually obtained, as in the incineration of the wood of plants. It therefore forms the base of this product,—the potash or pearlash of commerce, which also contains, however, other saline substances, particularly sulphate and muriate of potash, and earthy and metallic matter. From these, it is in part freed by dissolving the pearlash in an equal weight of warm water; the foreign substances being sparingly soluble, remain in a great measure undissolved; the clear liquor is poured off, and is evaporated until a pellicle appear on its surface; on cooling and remaining at rest for a few hours, it deposites a little muri-

ate of potash, and being poured off from this and evaporated, the sub-carbonate is obtained. The chemists have also employed other processes to procure it, such as burning tartar at a red heat: this substance consists of potash, combined with tartaric acid,—a vegetable acid having a compound base of carbon and hydrogen, and which, therefore, when decomposed by heat, affords carbonic acid, with which the potash combines. By deflagrating tartar with nitre, a similar product is formed, and also by deflagrating nitre with charcoal, the charcoal being converted into carbonic acid by the oxygen afforded by the decomposition of the nitric acid, and the carbonic acid combining with the potash, which is the base of the nitre. As obtained by these processes, the sub-carbonate of potash is even purer than in the state in which it is procured from the pearlash of commerce.

Sub-carbonate of potash, obtained in a concrete state by evaporation, is generally in the form of coarse grains, as it is not susceptible of regular crystallization. From the excess of alkali it contains, it is deliquescent; and if exposed to the air, it soon attracts as much water as dissolves it. Its taste is acrid; it changes the vegetable colours to a green, and combines with oils, forming a saponaceous compound. It is decomposed by the acids; its carbonic acid being disengaged with effervescence. A considerable portion, but not the whole of its acid is expelled by a strong red heat. It consists of about 60 of alkali, 28 or 30 of carbonic acid, and 6 of water, with a little siliceous earth, sulphate of potash, and argil.

Carbonate of Potash may be obtained by leaving the

solution of the sub-carbonate exposed to the air for a considerable time, carbonic acid being imbibed from the atmosphere, and thus crystals of the neutral carbonate are deposited. Or it is formed more directly by passing a current of carbonic acid gas through a solution of the sub-carbonate of such a strength that crystals form spontaneously. One part of the sub-carbonate dissolved in three of water affords a solution of the proper strength. The crystals are bevelled quadrangular prisms; they do not, like the sub-carbonate, deliquesce. They require, at a mean temperature, four parts of water for their solution, and produce, while dissolving, a degree of cold. They are much more soluble in hot water, the water taking up even $\frac{5}{6}$ of its weight; but if the temperature be that of boiling water, part of the carbonic acid assumes the elastic state, and rises through the liquor. The taste of this crystallized salt is more mild than that of the sub-carbonate, though still alkaline; it has no causticity, but it unites with oils, and changes the vegetable colours to a green: it can scarcely therefore be regarded as the neutral carbonate. It consists, according to its analysis by Pelletier, of 40 of potash, 43 of carbonic acid, and 17 of water. It is little used but for some medicinal purposes, but the sub-carbonate in the state of the potash and pearl-ash of commerce is applied to many uses in the arts, principally from the alkali it contains.

Potash is capable of combining with a less portion of carbonic acid, but still so as to form a crystallizable salt. It is also easily super-saturated by dissolving the sub-carbonate in water, (one ounce in ten pounds), and by the

assistance of cold and pressure impregnating the solution strongly with carbonic acid gas; the liquor, when a sufficient quantity of carbonic acid has been combined in it, is pleasantly acidulous, with some pungency, and the alkali thus super-saturated proves less irritating to the stomach than in any other state.

CARBONATE OF SODA.—The salt which usually receives this name is in strictness of nomenclature a sub-carbonate, for its taste is alkaline, and it changes the vegetable colours to a green. It is extracted from the saline matter obtained by the combustion of marine plants, the barilla of commerce; the purer kinds of barilla being lixiviated with warm water, and the solution being evaporated, so that on cooling it shall crystallize. The crystals are octohedrons; they are efflorescent, so as in a dry atmosphere to be soon reduced to a powder. They require, at a medium temperature, twice their weight of water for solution, and are more abundantly soluble in hot water, the saturated solution crystallizing on cooling. Exposed to heat, they suffer the watery fusion from the action of a large quantity of water of crystallization; as this is dissipated, the salt appears as a dry white powder, which by an increase of heat may be fused and partially decomposed. The proportions of the crystallized salt are 21.58 of soda, 14.42 acid, and 64 water of crystallization. Soda more fully saturated with carbonic acid may be obtained either by transmitting carbonic acid gas through a solution of the sub-carbonate, or, according to a process now received in the London Pharmacopœia, mixing one part of it with three parts of sub-carbonate of ammonia, the carbonic

acid of the latter salt being transferred to the soda, and the ammonia being distilled off. The residual liquor affords crystals of carbonate of soda. The alkali may also be super-saturated with carbonic acid by the same process as that followed with the carbonate of potash; and this super-saturated solution is like the other in medicinal use.

Carbonate of Ammonia.—Ammonia, by combination with carbonic acid in different proportions, affords various products, in which, however, the alkali is not altogether neutralized. Though they exist in a concrete state, they are volatile, retain the pungent ammoniacal odour and taste, and change the vegetable colours to a green. The combination is easily established; by presenting the two gases to each other, they instantly unite and form a concrete salt. It is more usually obtained, however, economically, in an indirect mode, by decomposing muriate of ammonia by carbonate of potash or lime.

Equal parts of chalk, dried, and of muriate of ammonia, are mixed together, and put into an earthen retort, or an iron pot, to which a capital is adapted, and which is connected with a large receiver. Heat is applied, by which a double decomposition is effected, the lime attracting the muriatic acid, and the ammonia, the carbonic acid. The muriate of lime remains in the vessel, and the carbonate of ammonia being volatilized, is condensed on the sides of the receiver in the form of a crust. Sometimes it is obtained by another process in solution in water. Equal parts of muriate of ammonia and of sub-carbonate of potash are put into a retort with two parts of water, and heat is applied; a double decomposition likewise

takes place in this case, the muriatic acid uniting with the potash, and the carbonic acid with the ammonia; the carbonate of ammonia passes over with the aqueous vapour, which, when condensed, is sufficient to dissolve it.

Carbonate of ammonia is also obtained in large quantity in the decomposition of animal matter by heat. It is thus procured from bones, and forms the impure product which has been named salt of Hartshorn.

The composition of these products varies so much, that, according to their analysis by Mr Davy, the quantity of ammonia is from 20 to 50 in 100 parts. The carbonic acid and water are super-abundant in it, as the temperature at which the compound has been formed is low; that formed at 300° contained he found above 50 of alkali, while that formed at 60° contained only 20; but in none of them is the alkali neutralized.

Sub-carbonate of ammonia is very soluble in water; at a mean temperature it requires only twice its weight, and at 212° less than its own weight is sufficient for its solution. Its saturated solution deposites crystals, the figure of which appears to be octohedral. Exposed to a very moderate heat, it is entirely volatilized, but is easily condensed, and its deposition on the sides of the vessel is of a regular dendritical form. It effloresces on exposure to the air, and its odour becomes weaker, perhaps from the loss of its moisture, or from the absorption of carbonic acid.

This salt is used in medicine as a stimulant and diaphoretic, and as a stimulating perfume.

Carbonate of Barytes exists native. When obtained by adding carbonic acid to barytic water, or by decomposing muriate of barytes by an alkaline carbonate, it is in the form of a white powder, of considerable specific gravity; is not soluble in water in any appreciable quantity, but is dissolved in small quantity when the water is impregnated with carbonic acid. This artificial carbonate is decomposed by heat, its carbonic acid being easily and completely expelled, owing, as has been supposed, to the presence of water which favours the transition of the acid to the elastic form; while in the artificial carbonate which contains less water, the decomposition is much more difficult; though by a heat sufficiently powerful, Dr Hope has shewn that it can be effected. The addition of a little carbonaceous matter favours the decomposition, by converting the carbonic acid into carbonic oxide.

Carbonate of Strontites is precipitated, on adding carbonic acid, or a solution of an alkaline carbonate, to a solution of strontites, or of a strontitic salt. With an excess of acid it becomes soluble. The artificial carbonate, like that of barytes, is more easily decomposed than the native.

Carbonate of Lime exists in nature in great abundance and under a variety of forms. It is formed artificially, by adding carbonic acid to lime-water; by agitating water impregnated with that acid with lime, or by decomposing any of the soluble salts of lime by any of the alkaline carbonates; but its chemical properties are generally described from those varieties of it which exist native in a state of purity. It is very sparingly soluble in water, and

in those forms of it in which the cohesion is considerable, appears altogether insoluble. By an excess of carbonic acid, solubility is communicated. When exposed to heat, it first loses what water it contains, and, if transparent and hard, becomes white, opaque, and friable. If the heat be augmented, the carbonic acid is expelled, and pure lime remains. This operation is performed on a large scale, on the different varieties of the native carbonate, marble, chalk, and more particularly limestone, to obtain lime for the numerous uses to which it is applied. The experiments of Sir James Hall have proved, that if the separation of the carbonic acid from its combination with the lime be prevented by the requisite pressure, the carbonate may be fused, and by a heat comparatively moderate, intermediate between 20° and 30° of Wedgwood's scale, according to the more or less perfect compression. A substance is thus formed, having considerable hardness and closeness of texture, and approaching by these qualities, as well as in fracture and specific gravity, to the finer kinds of limestone or marble. Bucholz has since discovered, that even without compression carbonate of lime is fused when it is submitted to heat in a large mass. The acids expel the carbonic acid from carbonate of lime, with effervescence; and this property of effervescing strongly on the contact of an acid, affords a discriminating character of carbonate of lime. The native carbonate perfectly pure, consists of 55 of lime, and 45 of acid.

CARBONATE OF MAGNESIA is prepared for medicinal use by dissolving equal weights of sulphate of magnesia and sub-carbonate of potash separately in twice their weight of

water; mixing them together, and immediately diluting with eight parts of warm water: the magnesia attracts the carbonic acid; and the compound being insoluble, is precipitated, while the sulphate of potash that is formed remains in solution. The mixture is made to boil for a few minutes: after cooling a little, it is poured upon a filtre: the clear fluid runs through, and the precipitate of carbonate of magnesia is washed with water till it is tasteless. When the process is conducted on the large scale, the bittern, or liquor remaining after the crystallization of sea salt, which is principally a solution of muriate and sulphate of magnesia, is substituted for the pure sulphate, and this is precipitated by a solution of pearlash, or of carbonate of ammonia procured by distillation from animal substances.

Carbonate of magnesia is perfectly white, nearly tasteless, possessing little coherence in its texture, and of a specific gravity not more than 2.3. It is very sparingly soluble in water; requiring at least 2000 times its weight, at the temperature of 60°. In this state, however, it is rather a sub-carbonate. When acted on by water impregnated with carbonic acid, it is dissolved; and from this solution allowed to evaporate spontaneously, the carbonate of magnesia is deposited in small hexagonal prismatic crystals, which are transparent and efflorescent: they are soluble in 48 parts of water, at 60°; and, by slow evaporation, this solution again affords crystals. These consist of 25 of magnesia, 50 of acid, and 25 of water; while the proportions of the common carbonate are, from 45 to 55 of earth, from 25 to 48 of acid, and from 15 to 30 of water.

Carbonate of Argil can scarcely be formed: water impregnated with carbonic acid dissolves a portion of the earth; but in evaporating the solution, the carbonic acid is expelled; and when an argillaceous salt is decomposed by an alkaline carbonate, the argil is precipitated, and retains little carbonic acid combined with it.

The other earthy carbonates are scarcely known. Carbonate of Zircon is insoluble. Carbonate of Glucine, obtained by double decomposition, is precipitated in a soft state, and is not easily dried; is insipid, insoluble in water, and is not rendered soluble by an excess of acid.

Water impregnated with carbonic acid dissolves small portions of some of the metals, particularly iron and zinc. By indirect modes it can be combined with the oxides of the other metals, forming compounds afterwards to be noticed.

Sect. V.—*Of Carbonic Oxide.*

Charcoal, in burning, combines with that proportion of oxygen which converts it into carbonic acid. But an intermediate product in the state of an oxide, it has been supposed, can be obtained by processes in which oxygen and charcoal are combined in a different mode, or in which carbonic acid is decomposed and its oxygen partially abstracted.

The processes in which the production of carbonic oxide was first observed, consist in exposing mixtures of

certain metallic oxides, particularly the grey oxide or scales of iron with charcoal to a red heat; a very large quantity of elastic fluid is disengaged, which consists partly of carbonic acid: but when this is abstracted by agitation with water, there remains an elastic fluid inflammable, and which, in burning, is converted into carbonic acid; it has hence been regarded as a gaseous oxide of carbon. On this hypothesis it must be supposed, that in its formation the oxygen of the metallic oxide has combined with the charcoal, and from the excess of charcoal present, has formed this oxide rather than carbonic acid.

There are other processes in which a product strictly analogous is obtained, from the partial decomposition of carbonic acid. Thus, if native carbonate of barytes, or dried carbonate of lime, be mixed with zinc or iron-filings, and exposed to a low red heat, there is an abundant production of elastic fluid: this contains a small portion of carbonic acid, but it consists principally of an inflammable gas, which, like the former, is converted into carbonic acid in burning, and towards the end of the process this gas is even disengaged perfectly pure. Its production, on the supposition that it is a pure oxide of carbon, must be ascribed to the metal abstracting a portion of the oxygen of the carbonic acid disengaged from the carbonate of barytes or carbonate of lime. And this decomposition, so as to afford this product, is established by another process still more direct,—passing carbonic acid gas repeatedly through an iron-tube, containing clean iron wire at a red heat; the iron is oxidated, and the carbonic acid, if the process is continued sufficiently long, is converted into carbonic oxide.

Some chemists, Berthollet in particular, have supposed that this gas always contains a portion of hydrogen, and is therefore a ternary compound, not a pure carbonic oxide. When obtained from processes in which charcoal is employed, the hydrogen, which there is some reason to believe exists in this inflammable substance, may enter into combination with the oxygen and carbon which form the elastic product; and accordingly the gas produced by this process has been observed, in burning, not only to form carbonic acid, but to deposite also a portion of water. In the processes in which it is obtained from the partial decomposition of carbonic acid, the hydrogen supposed to be contained in it must be derived from the small portion of water which that acid is supposed to hold combined.

There is considerable uncertainty with regard to the existence of hydrogen in well calcined charcoal, or the presence of combined water in carbonic acid, and hence it is difficult to form a decided conclusion with regard to this question. The production of a portion of water in the combustion of this gas is no proof that hydrogen is essential to its composition, for the hydrogen affording this may exist in the state of carburetted hydrogen merely mixed with it, and besides, as obtained by other processes, there is no deposition of water. Its production from the decomposition of the carbonic acid existing in carbonate of barytes, a compound in which the carbonic acid has been supposed to exist without even that small portion of water which the acid contains in its usual form, and its production also from carbonic acid gas, which has been previous-

ly exposed to the action of muriate of lime, so as to abstract any water, render more probable the conclusion that hydrogen is not essential to the constitution of this elastic fluid, and at least prove that the quantity of that element in its composition must be extremely small. It is therefore on the whole perhaps the most probable opinion, that it is an oxide of carbon.

There is one fact, however, rather singular with regard to this gas, which has been supposed favourable to the supposition that hydrogen is one of its elements,—this is its comparative levity. It is rather lighter than atmospheric air: oxygen gas is heavier: when combined with carbon, a heavier ingredient, it might, in retaining the elastic form, be expected still to become specifically heavier, and it actually does so in forming carbonic acid; yet, in increasing the proportion of carbon farther so as to form carbonic oxide, it becomes specifically lighter. This is an anomaly, which it has been supposed can be accounted for only on the supposition that hydrogen exists in the latter gas, and communicates its comparative levity. Some weight is due to this, yet there are some similar anomalies in other cases of chemical combination, and it cannot therefore be regarded as conclusive.

Carbonic oxide is permanently elastic. Its specific gravity is to that of atmospheric air as 967 to 1000. It is absorbed in small quantity by water, 100 cubic inches condensing 2 of the gas; but it has no acid taste, nor either in this condensed state or in its liquid form does it contract any union with the alkalis or earths. It burns with a blue lambent flame, but does not explode when previous-

ly-mixed with atmospheric air and kindled, nor does it combine with much oxygen; for although it is necessary to its complete combustion, that an excess of oxygen should be present, 100 cubic inches of it consume not more than 35 cubic inches of the oxygen gas. It forms a quantity of carbonic acid gas equal in weight to the carbonic oxide and oxygen consumed. From the products Cruickshank inferred that it consists of 21 of oxygen and 8.6 of carbon. Clement and Desormes state them at 58.4 of oxygen and 41.6 of carbon. The gas produced from the mutual action of charcoal and metallic oxides deposites a little water in burning, whence Cruickshank stated its composition at 15 of oxygen, 7 of carbon, and 1 of hydrogen. It is more probable, however, that it is the same with the other, and that the small quantity of hydrogen exists rather in the state of carburetted hydrogen mixed with the carbonic oxide.

SECT. VI.—*Of Oxy-carburetted Hydrogen Gases.*

THERE are obtained, in different processes, inflammable elastic fluids, which, in their combustion, afford carbonic acid and water in different proportions, and which appear, therefore, to be compounds of carbon, hydrogen, and oxygen, and as such may have the common name of oxy-carburetted hydrogen applied to them. There is, however, much difficulty in discovering their composition, especially with regard to the proportions of their constituent parts,

and it is even not easy to establish their specific distinctions, so as determine whether some of them are not mixtures of others. In this imperfect state of our knowledge on this subject, it will be sufficient to point out those of them which are afforded by uniform processes, and to state briefly their properties, and the best established facts with regard to their analysis.

If water be passed over charcoal in a tube raised to a red heat, a large quantity of elastic fluid is obtained, consisting partly of carbonic acid, and partly of an inflammable gas; the former having been formed by the combination of the oxygen of a portion of the water with part of the charcoal, the other from the combination of the hydrogen of the decomposed water with another portion of charcoal; the carbonic acid is abstracted by agitation with water; the inflammable gas remains. It has been named Carburetted Hydrogen, on the supposition that it is a compound of carbon and hydrogen. This, however, is very doubtful. The quantity of carbonic acid produced does not bear the due proportion to the quantity of inflammable gas which it ought to do, did the whole of the oxygen of the decomposed water enter into combination with carbon so as to form that acid; a portion of oxygen, therefore, enters into combination with the hydrogen and carbon, and the inflammable gas is thus a ternary compound of these elements. It accordingly deposites a quantity of water in its combustion; this, Cruickshank supposed, might have pre-existed in it, but the quantity is too large to admit of this supposition, especially as the carbonic acid produced must also hold a portion of water combined.

This gas has a specific gravity compared with atmospheric air as 11 to 23. It is inflammable, but less so than pure hydrogen; it burns with a blue lambent flame. 100 measures of it combine in burning with 66 measures of oxygen, and produce 40 of carbonic acid gas, with 9 grains of water deposited, besides the quantity which may be retained dissolved by the carbonic acid gas. It is extremely deleterious in its action on the living system when received into the lungs. An animal breathing it pure is almost instantly killed; and even when diluted with 20 parts of atmospheric air, it produces, when respired, sickness, vertigo, fainting, and other symptoms of exhausted power. It has the peculiar effect on the blood of giving to it a florid red hue.

Other elastic fluids, composed principally of carbon and hydrogen, with probably a proportion of oxygen, are disengaged in the decomposition of various vegetable products by heat. Thus, by passing the vapour of camphor through a red hot tube, one is obtained considerably heavier, and which, in burning, consumes more than double the quantity of oxygen, 100 cubic inches combining with 176 of oxygen gas, and forming 116 of carbonic acid gas, with 18 grains of water deposited. The vapour of ether or of alkohol passed through an ignited tube affords similar gases, rather lighter, however, and consuming in their combustion less oxygen. 100 cubic inches of the gas from ether combines in burning with 170 of oxygen gas, and afford 108 of carbonic acid with 18 grains of water deposited: of the gas from alkohol 100 cubic inches in burning combine with 118 of oxygen, and afford 75 of

carbonic acid gas with 13 of water deposited. The gas which arises from marshes, disengaged probably from the slow decomposition of vegetable matter, is similar to the gas from camphor or ether decomposed by heat; and Dr Henry has found, that the gas which collects in coal mines, and is known by the name of Fire Damp, is of a similar nature with an intermixture of carbonic acid gas and atmospheric air.

All these elastic fluids can be analysed by the operation of another powerful chemical agent upon them,—oxy-muriatic acid gas. If mixed with them condensation speedily takes place, and the whole is converted into water, carbonic acid, and muriatic acid: the oxy-muriatic acid, according to the theory which has usually been received of its composition, being a compound of muriatic acid and oxygen, and affording this oxygen to the hydrogen and carbon of the inflammable gas. A similar action is exerted, accompanied with detonation, when the electric spark is transmitted through the mixture of these gases. Carbonic oxide does not detonate with oxymuriatic acid gas, and this, independent of other characters, discriminates it from these gases, and farther renders it probable that no hydrogen exists in its composition.

An elastic fluid of the same family, but possessed of characters still more distinctly marked, is that which has received the name of Olefiant Gas. It is formed during the latter stage of the process of the formation of what is named Sulphuric Ether, by the action of sulphuric acid on alkohol at a high temperature; or it can be obtained directly, and in large quantity, by mixing three parts of sul-

phuric acid by weight with one part of alkohol, and submitting the mixture in a retort to a moderate heat. An effervescence is soon excited, the elastic fluid disengaged is the olefiant gas mixed with a portion of sulphurous acid gas; the latter is abstracted by agitation with water, and the former remains pure.

This gas derives its name from the singular chemical property it exhibits, that, when mixed with oxymuriatic acid gas, condensation of the two gases quickly takes place, and a liquid is produced from their mutual action, which collects first in a film on the surface of the water, and afterwards into globules having all the appearance of oil; it is rather heavier than water, and hence the globules soon sink; it is whitish and semi-transparent, has a smell somewhat aromatic and a sweetish taste. By agitation with water it is dissolved. The theory of its production is not very well ascertained; for it remains doubtful whether oxygen is communicated from the oxymuriatic acid to the entire principles of the olefiant gas, so as to convert them into this product, or whether it combines principally with its hydrogen, leaving the other principles in that state of combination whence it is formed. Mr Davy has found, that muriate of potash is formed by the action of potassium on it, and has supposed, therefore, that it may be a compound of oxymuriatic acid, carbon and hydrogen.

Olefiant gas has a specific gravity very nearly the same as atmospheric air, the difference being only as 909 to 1000. It has an odour slightly fetid; is absorbed in small quantity by water; it burns with a dense oily flame, and the emission of much light; and if previously mixed

with a sufficient quantity of atmospheric air or oxygen gas, detonates with much violence. Of any of these inflammable gases, it is the one which consumes the largest quantity of oxygen in its combustion, and gives the largest product of carbonic acid; 100 measures of it requiring, according to Dr Henry's experiments, 325 of oxygen for its perfect combustion, and producing 200 measures of carbonic acid. From its greater specific gravity compared with the other inflammable gases, it is evident that its principles are in a state of greater condensation; and from the large quantity of oxygen it consumes, it is also evident, that not much of that element exists in its composition, but that it must consist chiefly of carbon and hydrogen. Berthollet has supposed that it is composed of 75 of carbon and 25 of hydrogen.

Olefiant gas is disengaged in other processes, though not perfectly pure. It is formed by passing the vapour of alkohol either over ignited siliceous or argillaceous earth. From the gas which is disengaged in the decomposition of wood, and of some inflammable vegetable products by heat, burning with a dense oily flame, it is probably olefiant gas in a state of greater or less purity. It appears, too, that the gas disengaged from the bituminous matter of coal by heat, and which has been applied to the purpose of affording illumination by its combustion, is of a similar nature. It burns with a dense oily-like flame, even when it has been freed by washing from the bituminous matter suspended in it; and it consumes in burning, as Dr Henry has found, a very large quantity of oxygen gas, and affords a large product of carbonic acid. It appears, however, from his observations, not to be precisely the

same with the olefiant gas, though it is undoubtedly of analogous constitution. The gases disengaged from the decomposition of oil and of wax by heat are similar, and the flame they give in burning consists chiefly of this elastic fluid evolved by the heat, and in a state of combustion.

With regard to all the gases which have now been described, it may be remarked, in concluding their history, that it is not improbable that their chemical constitution is not uniform, but is liable to variations from the operation of the circumstances under which they are formed. Carbon, hydrogen, and oxygen, are principles having mutual affinities so equally adjusted, that they appear to be capable of entering into union in numerous, and perhaps in indefinite proportions, and the slightest variation of temperature, and of other circumstances, will have a material influence on their combination. The operation of such circumstances is accordingly conspicuous in the different nature of the elastic fluids disengaged in the above processes, from very slight differences in the processes by which they are procured. It is far from being improbable, too, as Dr Henry has remarked, that these gases may often be disengaged in a state of intermixture, by which they will appear to be still more diversified than they actually are. He has supposed, with Mr Dalton, that all these gases may be mixtures of two species, the Carburetted Hydrogen, obtained in the decomposition of water by charcoal, and the Olefiant Gas, with sometimes portions of carbonic oxide or pure hydrogen, but this is more doubtful.

CHAP. IV.

OF PHOSPHORIC ACID, ITS BASE, AND THEIR COMBINATIONS.

Phosphoric acid, by decomposition, affords phosphorus, a substance distinguished by its high inflammability, and which, so far as the processes of analysis have been carried, is the base of this acid, forming it by combination with oxygen. With a smaller proportion of oxygen, it forms Phosphorus Acid. With hydrogen it produces an elastic compound. It unites with sulphur and the metals, and is chemically acted on by the alkalis and earths.

Sect. I.—*Of Phosphorus.*

It was known to some of the alchemists, that a substance might be procured which burns spontaneously on exposure to the air. Kunckel made known the process by which they obtained it, that of distilling urine to dryness, and urging the solid residuum with a strong heat, the phosphoric acid existing in the salts of the urine being

decomposed, and its oxygen abstracted by the animal matter. By the addition of charcoal, this decomposition is facilitated: and the product is also increased, by an improvement introduced by Margraaf, that of adding a portion of muriate of lead, which, by abstracting the phosphoric acid from the soda and lime with which it is in part combined, allows it to be more easily decomposed.

Still the process was offensive and difficult; and phosphorus is now obtained with more facility, by decomposing phosphoric acid in a purer form. Scheele discovered, that the solid matter of bones, obtained by burning them to whiteness, is a compound of phosphoric acid and lime. This reduced to powder is submitted to the action of half its weight of sulphuric acid, diluted with from 10 to 20 parts of water, aiding their mutual action by the application of a moderate heat. The sulphuric acid exerts an affinity to the lime, and combines with a portion of it; the phosphoric acid, holding the remaining lime in combination, is obtained by lixiviating the materials with boiling water; the solution of super-phosphate of lime thus procured is evaporated to dryness; the dry mass is mixed with half its weight of charcoal powder, and the mixture is urged with a fire gradually raised in an earthen retort with a wide neck, to which a copper tube is adapted, the extremity of which dips in water; the charcoal attracts the oxygen of the phosphoric acid, and the phosphorus is volatilized and condenses, partly in the tube and partly in the water. The process, from the great inflammability of the product, requires considerable care. The phosphorus has a brown colour, from the presence of a small quantity

of carbonaceous matter, which is removed by straining it through leather when melted under warm water, or by digesting it with a little nitric or oxymuriatic acid. When melted under water it is run into moulds, so as to be formed into cylindrical pieces.

Phosphorus, when pure, is nearly colourless, and is semi-transparent. It has the consistence of wax, with rather more brittleness. Its fracture is often radiated, shewing a crystalline structure, and by slow cooling it can even be crystallized in octohedrons. It melts at 99° of Fahrenheit, is volatilized at 219°, and boil at 554°.

Exposed to atmospheric air it emits white fumes, and in the dark appears luminous,—appearances arising from its combustion. If heated to 100 this is brighter; and at 160 it burns with the emission of much heat and light. Its rapid combustion is also excited by friction without heat. In oxygen gas its combustion is extremely vivid, and the heat and light intense. A fact rather singular is, that the slow combustion at low temperatures does not take place in oxygen gas as it does in atmospheric air; the heat requires to be raised to above 80, or even to 100; and below 60, the phosphorus, if the oxygen is pure, has not even in the dark any luminous appearance. From the experiments made to determine the cause of this peculiarity, it appears, that the slow combustion of phosphorus in atmospheric air is an indirect process; the phosphorus is dissolved in small quantity by the nitrogen gas, and in this state being presented to the oxygen, combines with it: hydrogen gas has the same property of dissolving it, and hence a little nitrogen or hydrogen, added to oxygen

gas, in which phosphorus is placed, causes immediately the luminous appearance from the slow combustion.

The slow combustion of phosphorus in atmospheric air affords a very simple eudiometrical process. The air measured in a tube, divided into 100 equal parts, is transferred into another tube rather larger, in which it is exposed to the action of a cylinder of phosphorus, supported on a glass rod; the oxygen is gradually abstracted, and the product of the combination is absorbed by the water over which the air is confined. The diminution of volume is ascertained at the end of the experiment, by transferring the air into the graduated tube. This method is easy in the execution: the result is obtained in a few hours; and it has the advantage of indicating when the process is complete, the rise of white vapours from the phosphorus and its luminous appearance in the dark continuing while any oxygen is present, and ceasing when the whole of it has been abstracted. It requires only one correction; the nitrogen gas dissolving a small portion of phosphorus, receives from this an increase of volume, and hence the diminution with this method is never so great as with some of the others. The augmentation of volume amounts to about a fortieth; allowance is therefore to be made for this, so that if the residual gas, when the experiment has been made on atmospheric air, be equal to 80 parts, indicating an abstraction of oxygen equal to 20, the real volume is 78, indicating an abstraction of oxygen equal to 22.

Phosphorus is easily oxygenated by other substances. It burns in oxy-muriatic acid gas, and in nitric oxide gas,

and also in nitrous acid vapour, and receives oxygen from nitrous acid.

When saturated with oxygen, it forms a concrete acid, the Phosphoric. When the oxygenation is less perfect, what is named Phosphorous Acid is produced. The existence of an oxide of phosphorus has also been supposed, but is not clearly established.

Phosphorus forms with hydrogen an elastic compound, highly inflammable. Its compounds with sulphur in different proportions are likewise more inflammable than pure phosphorus. With charcoal it appears to form an imperfect combination. It unites with the greater number of the metals, and forms compounds retaining to a certain extent metallic lustre. With the metallic bases of the alkalis, it forms similar compounds. The alkalis and alkaline earths act upon it, and enable it to decompose water, whence phosphuretted hydrogen is produced.

Inflammable liquids, as alkohol, ether, and the oils, either expressed or volatile, dissolve phosphorus, especially when their action is aided by very moderate heat. The solutions in oils are luminous when exposed to the air, with scarcely any sensible heat. The solution in alkohol gives a vivid momentary illumination when dropped on water, and the phosphorus is precipitated from it.

Phosphorus has been regarded as a simple substance. Mr Davy, submitting it to the action of galvanism, found hydrogen to be produced from it in such quantity, that it can scarcely be considered as an accidental ingredient; and farther, finding that when acted on by potassium, the compound formed, when submitted to the action of an

acid, evolves less hydrogen than the same quantity of uncombined potassium would have done, he concluded that it contains oxygen, that it is a compound therefore of a substance unknown, with small quantities of oxygen and hydrogen. His subsequent researches have scarcely confirmed this, but have rather rendered it probable, that the phenomena whence the conclusion had been drawn arise from the presence of a little water in phosphorus.

SECT. II.—*Of Phosphoric Acid.*

PHOSPHORIC acid, obtained by the combustion of Phosphorus, is a flocculent substance of a white colour, which deliquesces on exposure to the air. The phosphorus, in burning, absorbs its own weight and a half of oxygen: the acid, therefore, consists of 60 of oxygen, and 40 of phosphorus.

Phosphoric acid is obtained most economically from the decomposition of the phosphate of lime of calcined bone, by sulphuric acid, by the process already described. To the solution of super-phosphate of lime, carbonate of ammonia is added, the ammonia of which combines with the phosphoric acid, forming phosphate of ammonia, which remains in solution, while the carbonate of lime, formed by the union of the carbonic acid with the lime, is precipitated: the phosphate of ammonia is procured solid by evaporation, and being exposed to a full red heat, the ammonia is expelled, and the acid is fused. It is still liable to retain

a minute portion of lime. It is therefore best obtained in a state of purity by the oxygenation of phosphorus. This is done either by the action of nitric acid, or simply by exposing sticks of phosphorus to the air, in a wide vessel, in which the vapours of the phosphorus acid, formed by the spontaneous combustion of the phosphorus, are condensed. A small portion of nitric acid is added to the liquid to complete the oxygenation, the water is evaporated, and, by raising the heat, the phosphoric acid may be fused. It then forms a glassy-like substance, nearly transparent, which, from exposure to the air, attracts humidity, and forms a liquid, dense, colourless, and inodorous.

Phosphoric acid has a high degree of acidity. Its affinities to the alkalis and earths are strong; and it exceeds the other acids, with the exception of the fluoric, in the power of neutralizing the alkaline properties. It does not act with much energy on the metals or inflammables, owing to the strength of affinity with which the oxygen is retained in combination with its base; but it combines with the metallic oxides. Its salts are named Phosphates. The alkaline phosphates are soluble and crystallizable, and melt into a glass. The earthy phosphates are in general insoluble.

Phosphate of Potash can scarcely be crystallized, but forms, by evaporation of its solution, a gelatinous mass, which attracts humidity from the atmosphere; its taste is saline, with a degree of sweetishness. Exposed to heat, it liquefies, and, after the expulsion of the water, is fused by the application of a red heat into a glass.

Phosphate of Soda, a salt employed in medicine, and for some chemical purposes, is prepared, by adding to the acidulous phosphate of lime, obtained from the decomposition of burnt bones by sulphuric acid, as much of a solution of carbonate of soda as may be sufficient to saturate the phosphoric acid; phosphate of lime is precipitated, and the water holding dissolved the phosphate of soda, is separated by filtration; by evaporation the salt is crystallized, its formation in regular crystals being promoted by a slight excess of alkali. The form of the crystals is a rhomboidal prism. They effloresce on exposure to the air, are soluble in three parts of cold water, and in half that quantity of boiling water. The taste of this salt being purely saline, without any bitterness, it has been introduced into the practice of medicine as a substitute for other aperient salts. As it melts easily, and promotes the fusion of the earths and metallic oxides, it is used as a flux, in analyses performed by the blow-pipe.

Phosphate of Ammonia is soluble in four parts of water at the temperature of 60; it crystallizes in prisms, which are neither efflorescent nor deliquescent. By exposure to heat, it is fused into a transparent glass, and decomposed, part of its ammonia being expelled. Heated with charcoal, its acid suffers decomposition, its oxygen being abstracted, which is not the case with the other phosphates. Like the phosphate of soda, it may be used with advantage in analyses by the blow-pipe. A triple compound of phosphoric acid, soda and ammonia is obtained from several of the animal fluids, and was known to the older chemists by the name of Microcosmic Salt.

Phosphate of Barytes is in the form of an insipid white powder, of considerable specific gravity: it is insoluble in water; is fusible at a high temperature; and is not decomposed by exposure to heat mixed with carbonaceous matter.

Phosphate of Strontites, when perfectly neutral, is very sparingly soluble in water, requiring about 2000 parts for its solution. It melts into an enamel by the flame of the blow-pipe; giving a phosphorescent light.

Phosphate of Lime, formed by decomposing the solution of an alkaline phosphate by muriate of lime, is in the state of a white powder, insoluble, and which is imperfectly vitrified by a very intense heat. It exists in the mineral kingdom under different forms, and is the base of calcined bone. When partially decomposed by an acid which exerts an affinity sufficiently powerful to lime, it is converted into a super-phosphate, which is soluble, and, by evaporation of its solution, crystallizes in silky fibres or in brilliant scales, which, by heat, are fused into a transparent glass.

Phosphate of Magnesia, formed from the direct combination of the acid and the earth, crystallizes in prisms which are efflorescent, soluble in about 50 parts of cold water, and in a smaller quantity of boiling water, and which by heat melt into a glass. Phosphate of Argil forms a white insipid powder: it melts before the flame of the blow-pipe into a transparent globule. Phosphate of Zircon is insoluble. Phosphate of Glucine is in the form of a white powder, or of a viscous substance, insipid, and insoluble in water, but rendered soluble by an excess of acid. It is melted by heat into a transparent vi-

treous globule. PHOSPHATE OF ITTRIA, formed by complex affinity, is insoluble, being thrown down in a gelatinous precipitate.

SECT. III.—*Of Phosphorous Acid.*

THIS acid is formed in the slow combustion of phosphorus in atmospheric air. It constitutes the white vapour which arises from the surface of the phosphorus, and which attracts water from the atmosphere, so as to be condensed, and forms a dense liquor, which has a smell slightly fetid, and a taste extremely sour. When exposed to heat, part of the water is volatilized; and as this proceeds, a vapour is formed, which, disengaged at the surface, affords a dense white smoke, attended even with a luminous appearance, visible in the dark, and, by continuing the heat until this ceases, the phosphorous acid is deprived of its peculiar smell, and is converted into phosphoric acid. From this experiment, some chemists have been disposed to consider phosphorous acid as merely phosphoric acid, holding a portion of phosphorus dissolved, the luminous vapour being probably phosphorus held in solution by the watery vapour. By longer exposure to the air, the acid passes slowly and imperfectly to the state of phosphoric acid. The change is effected more speedily by adding a little nitric or oxy-muriatic acid.

Phosphorous acid unites with the alkalis and earths, forming salts named Phosphites. These, in several of

their properties, resemble the phosphates. They are distinguished from the phosphates, by appearing luminous when heated by the blow-pipe, and by affording, by distillation, a small quantity of phosphorus. They detonate, too, with oxy-muriate of potash, and precipitate gold from its solution, in a metallic state. They pass very slowly into phosphates from exposure to the air. Those formed from the alkalis are soluble and crystallizable; those from the earths are insoluble, but acquire solubility from an excess of acid. They are so unimportant as not to require farther notice.

SECT. IV.—*Of Phosphuretted Hydrogen.*

THIS compound of phosphorus and hydrogen exists in the elastic form. It is obtained by combining with phosphorus a substance which, by a resulting affinity, shall enable it to decompose water. Thus, if one part of phosphorus is heated with 10 or 12 parts of a solution of potash, the alkali exerts this operation, one portion of the phosphorus combines with oxygen from the decomposition of the water, and forms phosphoric acid, with which the potash combines; another portion of the phosphorus is dissolved by the hydrogen of the decomposed water, and the elastic compound is disengaged. Another process is to combine phosphorus with dry lime, by causing the phosphorus to pass in vapour over lime inclosed in a tube, which is raised to a red heat. This phosphuret of lime

dropt into water instantly decomposes it, and phosphuretted hydrogen rises in the gaseous form, the lime favouring the action of the phosphorus on the water, as the potash does in the other process.

The distinguishing property of this gas is its high inflammability, in consequence of which it takes fire whenever it is presented to the atmospheric air. It cannot, with safety, be mixed with this air, even in small quantities; it is therefore merely allowed to burn as it escapes from the water in which the extremity of the retort containing the materials producing it is immersed. Presented in single bubbles to oxygen gas, its combustion is still more violent, and is accompanied with intense light. The products of the combustion are phosphorous acid and watery vapour, and a singular appearance is presented by these: the bubble of gas, as it escapes and inflames, expands into a horizontal ring of light white vapour, which enlarges in diameter as it rises, until it breaks; this is phosphorous acid wafted by the watery vapour, and it owes this form to the eccentric impulse of the explosion.

This gas is permanently elastic; it is sparingly soluble in water; its smell is fetid, very similar to that of putrid animal matter, though more faint. It has no sensible acidity. By remaining over water it is decomposed. From the products of its combustion, it is obvious that it is a compound of phosphorus and hydrogen; perhaps with a portion of oxygen. Its elements appear, too, to combine in different proportions; for the gas disengaged at the commencement of the process by which it is usually obtained, is not so highly inflammable as that which is afterwards formed.

Sect. V.—*Of Phosphuretted Sulphur.*

Sulphur and phosphorus combine by the application of heat, the mixture of them being usually heated under water to avoid the combustion of the phosphorus, and even the experiment in this way requires to be conducted with caution. The compound is more fusible than the phosphorus alone; its fusibility is greatest when it is formed from about equal parts, the mass remaining liquid at temperatures above 60°; in other proportions it is solid but soft. In its formation a portion of water appears to be decomposed; and when the heat is raised a little high, phosphuretted hydrogen is disengaged, and sometimes so rapidly as to produce an explosion. A portion of oxygen therefore probably exists in the composition of the compound. Dr Briggs has given a process in which the sulphur and phosphorus are combined in the dry way: heat being applied to them in a tube firmly corked by plunging it in warm water, and raising the heat gradually until the water boil.

Dr Briggs has observed, that this compound is different from that formed under water. When a small proportion of sulphur has been used, it is solid when cold, and has a crystallized appearance; the other is spongy and friable. The former is less inflammable than the latter, but is rendered equally inflammable by kindling it in the tube with a hot wire, and allowing it to burn for a few seconds, oxy-

gen probably being communicated to it from the air, or from the water formed by the combustion. Both are more inflammable than phosphorus, and hence these compounds are employed in forming the phosphoric match bottles; a very small proportion, however, of sulphur being added to the phosphorus, as with too large a quantity the compound is soft.

CHAP. V.

OF BORACIC ACID, ITS BASE AND COMBINATIONS.

THE salt named Borax has long been known in commerce, and applied to some uses in the arts. It is a native production brought from Thibet in an unrefined state. It consists of soda combined with a peculiar acid, which has derived from it the name of Boracic Acid. The acid is procured either by dissolving the borax in warm water, and adding sulphuric acid, which combines with the soda, and the solution on cooling deposites the acid in soft scales, which are freed from any adhering sulphuric acid or sulphate of soda by a second crystallization; or adding to sulphuric acid, diluted with an equal weight of water, two parts of borax in powder, and applying a moderate heat; the sulphuric acid combines with the soda, the boracic acid is volatilized by its affinity to the watery vapour, and condenses in scales in the neck of the retort.

Boracic acid has been decomposed, at least partially, by the application of galvanism, and by the action of potassium. When it is submitted to the action of a powerful galvanic battery, a dark coloured inflammable substance, Mr Davy found, is produced at the negative surface, which, when heated, burns slowly and reproduces acid matter. When the boracic acid was heated with an equal weight of potassium, vivid combustion was produced, and a substance obtained in the form of an olive coloured glass, which, when dissolved in water, deposited an olive coloured powder. This substance, exposed to heat, is neither fused nor volatilized, nor does it undergo much change except being rendered more dense. When heated under exposure to the atmosphere, it takes fire and burns with a red light; in oxygen gas it burns more vividly. In both cases boracic acid is formed. It is also oxygenated by nitric, sulphuric, and oxy-muriatic acids, and boracic acid is produced. It is not dissolved by hydrogen nor nitrogen: it combines with sulphur; and forms soluble compounds with the fixed alkalis. This substance, Mr Davy regards as standing in the same relation to boracic acid, that sulphur or phosphorus does to sulphuric or phosphoric acid, though it is probably not the simple base. In combining with potassium it forms a compound having a degree of metallic lustre, in which probably the pure base is contained. To this base Mr Davy assigns the name of Boracium; it may be metallic, and the olive coloured substance is perhaps an oxide. Gay Lussac and Thenard discovered the same inflammable matter, and ob-

served the different states of oxidation through which it passes before it forms the acid.

Boracic acid is in the form of white brilliant scales, soft to the touch; its taste is bitterish, with a slight degree of sourness; it reddens the vegetable colours. It is not altered by exposure to the air; is soluble in 20 parts of cold water, and in 5 of boiling water. It is also soluble in alkohol, and, what is a distinctive character of it, gives to the flame of alkohol in burning a green colour.

Exposed to a moderate heat it swells; when the heat is raised to redness, it is fused into a glass, which is soluble again in water. By the most intense heat it is not volatilized; but if water be present, the aqueous vapour elevates with it a portion of the acid.

Boracic acid combines with the alkalis and several of the earths, forming compounds named Borates. These retain the property of communicating a green colour to the flame of alkohol. They are decomposed by all the acids, the carbonic excepted, in the humid way; but in the dry way, the boracic acid, from its great fixity, is able at a high temperature to decompose those salts, the acid of which has a tendency to assume the gaseous form. The alkaline borates are very soluble in water, while the earthy are the reverse.

Borate of Potash, like the other borates, has a tendency to form with an excess of alkali; it is soluble in water; by slow evaporation its solution affords prismatic crystals, which are not changed by exposure to the air. It is fused into a glass by heat.

Borate of Soda, the Borax of Commerce, is a native

production, being obtained from a lake in Thibet, from the sides of which it is dug up, and where there appears to be a constant reproduction of it. In the state in which it is imported, it is impure, but is purified by calcination, solution and crystallization. In the state in which it is met with in the shops, it is in the form of crystalline masses, of a figure irregular, but approaching to an hexaedral prism. It is not perfectly neutral, but contains an excess of soda, which seems necessary to cause it to crystallize, the solution of the neutral salt forming by evaporation a gelatinous mass: it is soluble in 12 parts of cold, and in 6 parts of boiling water; it is very slightly efflorescent, when exposed to a moderate heat, it melts from the water of crystallization it contains; when this is evaporated, there remains a spongy white mass, named Calcined Borax. If the heat be raised to ignition, this is melted into a pellucid glass which suffers no decomposition. It is decomposed by the greater number of the acids and by potash and the earths, the former uniting with its alkali, the latter with its acid. From the facility with which it melts and brings other substances into fusion, it is of use in some arts, as in making of glass, especially the finer glass for imitating the gems, in assaying minerals by the blowpipe, and in soldering the more valuable metals.

Borate of Ammonia, though little known, has been described as being obtained by evaporation of its solution in prismatic crystals, of a sharp taste, and which change the vegetable colours to a green, evidently, therefore, containing an excess of alkali.

BORATE OF BARYTES.—This compound, formed by adding boracic acid to barytic water, is precipitated in the form of a white powder, insipid, and insoluble.—BORATE OF STRONTITES forms a similar precipitate, which appears, however, to have an excess of base, and which dissolves in 130 parts of boiling water.—BORATE OF LIME is precipitated in the state of an insoluble powder, white and insipid.—BORATE OF MAGNESIA is obtained by evaporation, in a crystalline mass, of no regular form. With the addition of lime, it forms a mineral substance, known by the name of Boracite. It occurs crystallized, in cubes, which are so hard as to scratch glass; semi-transparent; of a white colour, with a shining lustre.—BORATE OF ARGIL is obtained by evaporation of its solution, in the form of a viscid substance, through which minute crystals are interspersed, having a very astringent taste.

Boracic acid acts very feebly on the metals, but may be combined with their oxides by a complex affinity.

CHAP. VI.

OF FLUORIC ACID, ITS BASE AND COMBINATIONS.

THIS acid exists in the mineral known by the name of Fluor Spar, in which it is combined with lime, and from which it was obtained by Scheele, who made known its

principal properties. It has since been discovered in a few other minerals; and the discovery, rather unexpected, has more recently been made, that it exists in the animal kingdom, particularly in the enamel of the teeth, and in the fossil or petrified teeth of the elephant.

It was ranked as one of the undecomposed acids, its base being altogether unknown. By the action of potassium, however, on it, phenomena have been produced, indicating its decomposition.

When potassium is heated in fluoric acid gas, Mr Davy found that it burns; a great portion of the gas disappears; and if a sufficient quantity of potassium has been employed, the residual gas is hydrogen, and the quantity of it is less as the acid gas has been more free from water. A substance of a chocolate colour is formed. This burns when heated in atmospheric air, or in oxygen; oxygen is absorbed, and acid matter formed. It may be concluded, therefore, that it contains the base of the fluoric acid; but it is probably not this base in a pure state, but in a state of oxidation combined with potassium. Experiments with results nearly similar were performed by Gay Lussac and Thenard.

To obtain fluoric acid, fluor spar in coarse powder is submitted to the action of twice its weight of sulphuric acid. The operation must be performed in a leaden retort, from a singular property of this acid, that it dissolves siliceous earth, and hence acts on glass. The sulphuric acid combines with the lime of the fluor spar, and the fluoric acid assumes the gaseous form. The gas may be collected over mercury, as it is absorbed by water; or if it

is to be condensed, the retort is connected with a leaden receiver, containing a sufficient quantity of water. Yet it is difficult to obtain it pure; it is liable to have a slight contamination of lead, and a portion of silex often adheres to it, derived from the fluor spar. From this it may be freed, by saturating it with an alkali, and decomposing this compound by an acid.

Fluoric acid gas is permanently elastic, and heavier than atmospheric air; it has a pungent suffocating odour, is corrosive, and highly acid. It has a strong attraction for water, so that when presented to the atmosphere, white vapours are immediately formed from its attracting the watery vapour; and when dry, it takes water, as Gay Lussac and Thenard have remarked, from almost every other gas. When transparent, however, it does not appear to retain much combined with it. It is largely absorbed by water, and the liquid when saturated is highly acid and caustic; it emits white vapours, but the whole of the acid gas cannot be expelled from it. Either in the gaseous or liquid state, it does not act very powerfully on the metals or inflammables.

It combines with the alkalis and earths, forming salts named Fluates. They are generally deliquescent, and not easily crystallized: the fluoric acid, in power of neutralizing the alkaline properties, exceeds the other acids: hence, if this be admitted as the test of the strength of acidity, it is the most powerful of the acids, and its apparently less energetic action is to be ascribed to its not being obtained liquid in a sufficient state of concentration.

Fluate of Potash is very soluble in water, and its so-

lution evaporated does not crystallize, but becomes gelatinous, or forms a foliated mass, which, when urged by heat, is melted and decomposed.—Fluate of Soda has scarcely so much affinity to water; it affords, when evaporated to the consistence of honey, small oblong crystals.—Fluate of Ammonia, when in solution, becomes gelatinous on evaporation, and in this jelly crystals form which are deliquesent, melt on exposure to heat, and are sublimed with partial decomposition.—Fluate of Barytes being considerably more soluble than fluate of lime, this acid has been employed as a test to discriminate between these two earths.—Fluate of Strontites being of sparing solubility, is precipitated when it is formed.—Fluate of Lime, in its native state, forms the Fluor Spar, which is often regularly crystallized. Obtained by digesting liquid fluoric acid on lime, it is in a very different state: the solution, even when evaporated to a jelly, does not afford crystals. It is insipid, and insoluble in water. It is phosphorescent from heat, a property which belongs also to the native fluate. It is fused, by a violent heat, into a transparent glass.—Fluate of Magnesia, obtained in solution, by digesting fluoric acid on magnesia, is gelatinous.—Fluate of Argil does not crystallize, but assumes on evaporation the consistence of a jelly; its taste is astringent.

Fluate of Silex is a compound so singular as to require more distinct notice, this earth being scarcely acted on by any other acid in the humid way. It combines with the fluoric acid, either when the acid in its gaseous state, or combined with water, is brought to act on it, or

on almost any compound containing it. Thus, when the acid is disengaged from fluate of lime, if the experiment be made in a glass-vessel, part of the silex of the glass is dissolved; or if a little flint in powder has been mixed with the materials, the fluoric acid gas holds dissolved a large portion of silex. It retains it in solution, when received over quicksilver; but when presented to water, a considerable portion is separated, and forms a gelatinous matter, retaining a little acid; and the acid, absorbed by the water, has a portion of the earth combined with it. If the liquid fluoric acid be kept in a glass-vessel, it acts slowly upon it; or if digested with quartz or flint in powder it becomes impregnated with silex, and after a length of time crystals are deposited, which are affirmed to be fluate of silex. From the strong affinity of this acid to silex, it retains a portion of it in combination with other salifiable bases, forming ternary compounds; or if previously combined with these bases, it still acts on and dissolves a portion of siliceous earth. The acid from this power is employed to engrave on glass, being applied either in the gaseous or liquid form.

CHAP. VII.

OF MURIATIC ACID, OXY-MURIATIC ACID, AND THEIR COMBINATIONS.

From Sea Salt, an acid is procured by distillation with sulphuric acid, formerly known to chemists by the name of Spirit of Salt, now named Muriatic Acid. It exists as a permanent gas, but is condensed by water in very large quantity, and forms a liquid acid of considerable strength.

This acid resists the usual methods of chemical analysis, and its composition, therefore, was altogether unknown. Girtanner had supposed hydrogen to be its base, from finding that this element is evolved when it is submitted to the action of oxidiable bodies; and on similar grounds Berthollet supposed it to have a compound base of hydrogen and nitrogen,—conjectures not supported on any decisive evidence, as any relation which it apparently had to hydrogen might be accounted for from the portion of water combined with it.

More lately, some singular facts have been established with regard to the influence of water in combination with muriatic acid, and these have even suggested to Mr Davy a very different view of the constitution of this acid. On obtaining the acid gas as dry as possible, and heating potassium in it, there is a violent chemical action

with ignition; the acid gas wholly disappears; more than one-third of its volume of hydrogen gas is evolved; and on the supposition that this is derived from water contained in the muriatic acid gas, there is reason to infer, that the acid in its common aëriform state must contain one-third of its weight of water. Mr Davy farther found, that muriatic acid could not be disengaged from its dry combinations by other concrete acids, from muriate of lime, for example, by dry phosphoric or boracic acid, by the application of heat; but if water were added, it is extricated in large quantity,—an experiment which apparently proves the necessity of water to the constitution of muriatic acid gas. Similar results had been obtained by Gay Lussac and Thenard. It had also been known, that when muriatic acid is subjected to the action of the electric spark, hydrogen is evolved, and this, even when the gas had been previously rendered as dry as possible, by being exposed to substances which have a strong affinity to water.

All these facts may be explained on the hypothesis that muriatic acid contains water in a state of intimate combination; but Mr Davy has, from other speculations, been led lately to give a different theory of them. In submitting muriatic acid to the action of substances which afford oxygen easily, it is converted into a substance which, being supposed to be a compound of muriatic acid and oxygen, has been named Oxy-muriatic Acid. This conclusion Mr Davy has called in question: oxy-muriatic acid he regards as a simple body, and muriatic acid as a compound of it with hydrogen. The grounds on which this last conclusion rests, being connected with the theory of

the constitution of oxy-muriatic acid, will be best stated under its history.

Muriatic Acid is always obtained from sea-salt decomposed by sulphuric acid, one part of the acid being added to two parts of the salt. The sulphuric acid combines with the soda, which is the base of the salt; and the muriatic acid, which is the other ingredient, is disengaged, and assumes the elastic form. The gas may be received over quicksilver, as it is largely and rapidly absorbed by water; or if it is to be procured in the liquid form, the retort containing the materials is connected with the bottles of Woolfe's apparatus, in which water is placed, by which its condensation is effected, a moderate heat being applied, by the medium of a sand-bath, as long as any acid is produced. When the process is carried on on the large scale, the distillation is facilitated by diluting the sulphuric acid with a portion of water.

Muriatic acid gas, when free from watery vapour, is transparent and invisible; it is pungent and suffocating; its specific gravity is, to that of atmospheric air, as 1929 to 1000. It extinguishes combustion, and does not burn. By water it is instantly condensed in very large quantity, the water absorbing not less than 360 times its volume of the gas, by which its weight is doubled; and this absorption is attended with a rise of temperature. Ice melts in it, condenses it, and produces cold.

In the liquid muriatic acid obtained by the usual process of distillation, the water is not completely saturated with the gas; its specific gravity seldom exceeds 1.170, and the strongest that can be easily procured is that of

1.196: when of this strength, it contains, according to Kirwan's estimate, 25 of real acid. In its common state it has a yellow tinge, but this arises from impurity; and by distilling it from a little muriate of soda, it is obtained colourless. It emits white vapours, having a pungent smell, and, even when largely diluted, has a very sour taste, and reddens the vegetable colours. As it does not directly communicate oxygen, it does not act with much energy on inflammable substances; and it dissolves metals only by enabling them, by the resulting affinity it exerts, to decompose water and attract its oxygen; hence these solutions are attended with a disengagement of hydrogen gas. It combines with all the metallic oxides; it also unites easily with the alkalis and earths. Its salts are named Muriates; the alkaline and earthy muriates are soluble and crystallizable, and have in general that taste more peculiarly denominated saline.

Muriate of Potash has a taste saline and slightly bitter; it is soluble in three parts of cold, and in half its weight of boiling water, the latter solution crystallizing on cooling; its crystals have a cubic form, but are not regular: they are slightly deliquescent, and they decrepitate when heated. This salt, obtained by some indirect chemical processes, is used in the manufacture of alum, and as a flux in melting some of the metals.

Muriate of Soda is the salt which exists in largest quantity in nature. It is the principal saline ingredient of the ocean, forming, when it is extracted, what is named Sea Salt, and it exists in immense beds in the earth forming Rock Salt. In the latter, it is generally pure, or has

only a slight contamination. In the former it is less pure, a portion of other salts adhering to it, greater or less according to the method in which it is procured. In warm climates it is frequently obtained by spontaneous evaporation, the sea-water being admitted into shallow trenches by the sea-side, and spread over an extensive surface: as it becomes concentrated by the evaporation of the water, the liquor is removed, by sluices, from one trench to another, until at length the muriate of soda crystallizes spontaneously, and with scarcely any intermixture of the other salts. In colder climates, the sea-water is evaporated in large boilers by the direct application of the heat, and the evaporation is carried so far, that the muriate of soda concretes in small crystals on the surface of the boiling liquor: as obtained by this mode, a small portion of muriate and sulphate of magnesia adheres to it, which render it slightly deliquescent, and somewhat impair its antiseptic power. The processes of spontaneous and hasty evaporation are sometimes conjoined, and a salt of intermediate purity is obtained.

Muriate of soda crystallizes by slow evaporation in cubes; it has a saline taste with scarcely any bitterness; is soluble in less than three parts of cold water, and its solubility is very little increased by raising the temperature even to 212°; hence it crystallizes from its solution, not by cooling, but only by slow evaporation. Its crystals neither deliquesce nor effloresce; they decrepitate when suddenly exposed to heat, the water of crystallization being dissipated in vapour; the salt melts at a red heat, and at a more intense heat is volatilized without decom-

position. It is decomposed by the fixed acids, which expel the muriatic acid, especially when aided by heat.

Muriate of soda is in common use to counteract the process of putrefaction in animal matter, and the theory of its antiseptic operation is not well understood: it is taken universally as a condiment to food, and it is employed in a number of chemical arts. The decomposition of it, so as to obtain its alkaline base, is a process of much importance, as affording a source whence soda can be abundantly procured. It has been attempted on the large scale by the intermedium of oxide of lead, of carbonate of potash, of lime and iron, of sulphuric acid, and the sulphate of soda being afterwards decomposed by the joint action of iron, lime, and charcoal; some of these processes are, from local circumstances, frequently carried on with advantage.

Muriate of Ammonia.—This is the sal-ammoniac of commerce, an important salt from the uses to which it is applied, and which is generally prepared on a large scale. The processes are various, but in general a sulphate of ammonia is procured by maceration from soot, or by saturating the impure ammonia obtained in the distillation of animal substances by adding sulphuric acid; it is decomposed by muriate of soda, and the muriate of ammonia, formed by the operation of a double affinity, is sublimed. It is thus obtained in large semi-spherical cakes of a crystalline structure. By solution in boiling water and cooling it may be crystallized, its crystals being four-sided prisms. It is soluble in $3\frac{1}{2}$ parts of water at 60°, and in its own weight of boiling water. It is volatilized by heat. It is used in soldering the metals, and in

some of the processes of dyeing; and it is from this salt that ammonia is usually procured.

Muriate of Barytes is soluble in three parts of cold water, and in a smaller quantity of hot water; it crystallizes from the latter solution on cooling in quadrangular tables. It is also soluble in alkohol.—Muriate of Strontites is so soluble as to require not more than its weight of water at 60° to dissolve it: in boiling water it is still more soluble, and it crystallizes from this solution on cooling in slender six-sided prisms: its crystals are deliquescent.—Muriate of Lime is also extremely soluble, and, from its strong affinity to water, imbibes it rapidly. By cooling its saturated solution, it may be obtained crystallized in six-sided prisms; these crystals are so deliquescent that they are not easily obtained dry, they liquefy on exposure to the air, and they combine rapidly with ice or snow, causing it to melt, and thus producing intense cold.—Muriate of Magnesia has such an affinity to water that it can be obtained in acicular crystals only by exposing its concentrated solution to sudden cold: these crystals are very deliquescent, and dissolve in less than their weight of water: the taste of this salt is extremely bitter.—Muriate of Argil can scarcely be crystallized, its solution becoming gelatinous on evaporation; it has the astringency of the other argillaceous salts.—Muriate of Glucine is soluble in water, and, by evaporation, can be obtained in small crystals.—Muriate of Zircon is also soluble, and affords, by evaporation of its solution, transparent needle-like crystals.—Muriate of Ittria assumes a gelatinous form. On Silex muriatic acid appears to exert some action, as, when this

earth is newly precipitated, it is sensibly dissolved by the addition of the acid.

A compound acid is formed by the mixture of muriatic acid and nitric acid, which has some peculiar properties, and which in particular dissolves gold with facility,—a property from which it received from the alchemists the name of Aqua Regia. It is obtained by mixing one part of muriatic with two parts of nitric acid; during their combination the formation of oxy-muriatic acid is indicated by its odour, nitric oxide gas is disengaged, and a portion of it is also retained in the liquid, giving it a dark orange colour. It has been concluded, therefore, that in the mutual action of these acids, part of the nitric acid is decomposed, its oxygen is transferred to the muriatic acid, and to the oxy-muriatic acid thus formed the peculiar powers of the compound have been ascribed. It appears, however, to be chiefly a compound of nitric and muriatic acids, and its energetic action on the metals appears to be owing to the latter acid by a disposing or resulting affinity promoting the decomposition of the former, favouring therefore the communication from it of oxygen to the metal, with which in its oxidated state it then combines. It is named Nitro-muriatic Acid, and is employed in some of the processes of assaying.

SECT. II.—*Of Oxy-muriatic Acid.*

SCHEELE discovered, that in the action of muriatic acid on black oxide of manganese, the acid sustains very important changes in its properties. A gas is disengaged of a greenish yellow colour, having an intolerable suffocating odour, not so easily condensed by water as muriatic acid gas, having much less acid power, and peculiarly distinguished by the property of destroying the vegetable colours. According to the views of chemical theory then adopted, he concluded, that this change is produced in muriatic acid by phlogiston being attracted from it by the black oxide of manganese. He therefore named it Dephlogisticated Muriatic Acid.

This theory, expressed according to the language of the more modern chemical system, implied merely, that the muriatic acid received oxygen. The new product, therefore, was named Oxy-muriatic Acid, and this view of its constitution appeared to be confirmed by other facts. The oxide of manganese, on which it had acted, was found to be deprived of much of its oxygen: when the acid was submitted to the action of substances having an attraction to oxygen, as, for example, to the metals, these were found to be oxidated; while muriatic acid was at the same time reproduced: by the simple experiment even of exposing the solution of the oxy-muriatic acid in water to the rays of the sun, very pure oxygen gas was found to be produced, accompanied with the transition to muriatic

acid; or, lastly, if the oxy-muriatic acid were combined with alkaline bases, these compounds afforded a large quantity of pure oxygen when decomposed by heat, and in this case too muriatic acid was obtained. All these facts appeared to prove unequivocally, that the product of the action of muriatic acid on oxide of manganese is a compound of that acid with oxygen, and, in conformity to this, it was farther found, that it might be formed by the action of muriatic acid on other substances capable of affording oxygen.

Notwithstanding the apparent strictness of these conclusions, they have lately been called in question by Mr Davy, and the opposite theory has been advanced, that oxy-muriatic acid contains no oxygen, but, so far as our knowledge of it extends, is a simple substance belonging to the same class with oxygen, or possessed like it of the property of communicating acidity to the combinations into which it enters. He was led to doubt of the existence of oxygen in oxy-muriatic acid gas, from finding, that charcoal, if free from hydrogen, heated in it, produces no change, though, as this inflammable has so strong an attraction to oxygen, it ought to abstract it if it existed in the oxy-muriatic acid, especially as the oxygen has been supposed to be retained in this acid by a weak affinity. When hydrogen gas and oxy-muriatic acid gas are presented to each other, they are converted into muriatic acid: according to the common theory, this must be supposed to arise from the combination of the oxygen of the oxy-muriatic acid with the hydrogen, forming water. But Gay Lussac and Thenard have found, that no water is deposited in the experiment. Mr Davy farther found,

that oxy-muriatic acid forms combinations with inflammables and metals; but in these compounds, while water was excluded, he could discover no indication of the presence of oxygen. He remarks, therefore, that there is no experimental evidence of the existence of oxygen in oxy-muriatic acid; and the direct inference from the production of muriatic acid by the mutual action of oxy-muriatic acid and hydrogen is, that it is a compound formed by their combination. On this hypothesis may be explained all the facts whence the common theory of the constitution of oxy-muriatic acid has been inferred.

This view, singular as at first it appears to be, may no doubt be maintained; yet the opposite theory, I would remark, may still be defended, and the investigation of this important subject is not yet sufficiently advanced to admit of any certain conclusion being drawn. Its relation to the general theory of acidity has been already considered.

THE process employed by Scheele to obtain oxy-muriatic acid, consists in distilling with a moderate heat muriatic acid diluted with an equal weight of water from black oxide of manganese. It is more economical, and succeeds equally well to mix with the oxide, muriate of soda and sulphuric acid; four parts of muriate of soda being taken with one of black oxide, and three of sulphuric acid previously diluted with two of water. Their mutual action is favoured by a very gentle heat. The sulphuric acid combines with the soda of the muriate of soda, and disengages the muriatic acid, which, according to the common theory,

receives oxygen from the black oxide of manganese, or, according to the hypothesis of Davy, the oxygen of the oxide combines with the hydrogen of the muriatic acid and forms water, while the other principle of the acid, the Oxy-muriatic Acid as it is named, is disengaged.

The oxy-muriatic acid produced in this operation is disengaged in the elastic form, and if it is to be submitted to examination under this form, it may be received over warm water. It may be condensed by passing it through cold water in the bottles of Woolfe's apparatus, and may thus be procured in the liquid form.

Oxy-muriatic acid gas, though it retains its elasticity at low temperatures under a common atmospheric pressure, may be condensed by applying powerful pressure to it. It is the only gas that is visible, being discovered by its yellowish green colour; it is heavier than atmospheric air; its odour is intolerably suffocating, and even when largely diluted with atmospheric air it produces a sense of suffocation when it is respired.

It is absorbed by water in a quantity larger as the temperature is low; at 50° the water takes up about twice its volume. When the water is saturated with it, if it be cooled below 40° it suffers a kind of congelation, soft scales are formed in it, and even crystals in the form of quadrangular prisms; these are the compound of the oxy-muriatic acid and water: a moderate heat soon liquefies it. The solution has a yellowish green colour, and its odour is that of the acid itself; its taste is rather styptic than sour, and, like the gas itself, it has the property of destroying the vegetable colours.

Liquid oxy-muriatic acid is decomposed by exposure to light, pure oxygen gas being disengaged, and muriatic acid produced. According to the common theory, this is owing to the separation of the oxygen from its combination with the muriatic acid: according to the theory advanced by Mr Davy, it must be supposed owing to the hydrogen of part of the water combining with the oxy-muriatic acid, and forming muriatic acid, while the oxygen of the decomposed water appears in the elastic form. From the quantity of oxygen given out during the exposure to the solar light, compared with the quantity of muriatic acid found to be in the residual liquid, Berthollet inferred, that 100 parts of oxy-muriatic acid consist of 89 of muriatic acid and 11 of oxygen. Chenevix, from the products of the decomposition by heat of the salt which oxy-muriatic acid forms with potash, concluded, that the proportions are 84 of muriatic acid, and 16 of oxygen.

Oxy-muriatic acid gas supports the combustion of a number of inflammable substances. A lighted taper burns in it; phosphorus takes fire when immersed in it, and a number of the metals, as antimony, arsenic, copper, or others, if introduced into it in leaves or filings, burn spontaneously. For the success of the experiment the gas must be pure, and the temperature above 70°. In these combinations it has usually been supposed that the oxygen of the oxy-muriatic acid is combined with the inflammable or metallic substance, and that with this the muriatic acid combines. According to Mr Davy, compounds are formed of the inflammables or metals with oxy-muriatic acid; it is only when water is communicated to them that oxygen is afforded, the oxygen of the water being transferred to the

inflammable or metallic base, while the hydrogen forms with the oxy-muriatic acid, muriatic acid which unites with the oxide.

Hydrogen and oxy-muriatic acid gases act on each other very slowly at a low temperature, unless water be admitted, which favours their mutual action. If the electric spark be transmitted through the mixture of them they disappear, and muriatic acid gas is produced. Dalton and Gay Lussac have also observed, that a similar rapid combination is produced when they are exposed to solar light. Carburetted and sulphuretted hydrogen gases are decomposed by it, and it decomposes ammonia.

Sulphur, if introduced in fusion, burns in oxy-muriatic acid gas; if not in fusion it combines with it, and forms a liquor of a red colour, which Dr Thomson, who observed its production, has considered as a compound of oxide of sulphur and muriatic acid. Mr Davy supposes it to be a compound of oxy-muriatic acid and sulphur.

In its liquid form oxy-muriatic acid does not act with much energy on inflammables. Some of the metals, however, are dissolved by it, oxygen being previously communicated to the metal either from the acid or the water.

The most important chemical property of this substance is displayed in its action on the vegetable colours. Many of them it entirely destroys; and even those which are most deep and permanent, such as the colour of indigo, it renders faint, and changes to a light yellow or brown. Berthollet applied this agency of oxy-muriatic acid to the process of bleaching, and with such success as to have entirely changed the manipulations of that art. The method of applying it has been successively improved. It

consisted at first, in subjecting the thread or cloth to the action of the acid in the gaseous form, but the effect in this way was unequally produced, and from the too powerful action of the acid gas, the strength and texture were sometimes injured. It was then applied, condensed by water, and in a certain state of dilution, the thread or cloth being prepared by previous boiling in water, to extract as much as possible of its colouring matter, being then boiled in a weak solution of potash, and afterwards immersed for a few hours in the diluted oxy-muriatic acid; and thi- alternate application of the acid and alkali being continued until the colour was discharged. To avoid the offensive suffocating odour of the acid, the improvement was introduced of condensing the acid gas by a weak solution of potash: lime diffused in water being more economical, was afterwards substituted; even slaked lime in the state of powder has been employed, the compound it forms with the acid being dissolved in water, so as to form the bleaching liquor of the proper strength. Under all these forms the oxy-muriatic acid was supposed to produce the bleaching effect, by imparting oxygen to the colouring matter: the colour by this oxygenation is weakened, and the colouring matter is at the same time supposed to be rendered more soluble in the alkaline solution, alternately applied, and of course more easily extracted by its action. More lately, the improvement has been introduced of employing the potash alone, its solvent power being aided by applying it with the steam of water, at a high temperature under increased pressure.

The relation of oxy-muriatic acid to the alkalis and earths is peculiar. When presented to the alkali in a

concentrated state, it does not directly combine with it, but undergoes decomposition; a portion of it returns to the state of muriatic acid, and the other portion, with a quantity of oxygen, enters into combination with part of the alkaline base. It has been concluded from this, that no combination of the oxy-muriatic acid with the alkalis exists. This appears, however, to be a mistake: when the acid and the alkaline solution are much diluted, their mutual action is rendered less energetic: this decomposition, therefore, does not take place, but their direct combination is established; the proof of which is, that the liquor thus formed retains the characteristic property of oxy-muriatic acid, that of weakening or destroying the vegetable colours. These combinations, however, cannot be obtained in an insulated state, as there is no mode of concentrating their solution without giving rise to that re-action which produces decomposition.

SECT. III.—*Of Hyper-oxymuriatic Acid.*

WHEN a current of oxymuriatic acid gas is passed through an alkaline solution of a certain strength, a salt is deposited by spontaneous crystallization, which, by analysis, is found to contain a larger portion of oxygen, compared with the quantity of muriatic acid it contains, than it could do, supposing it to be a compound of oxymuriatic acid. It has also been found, that a portion of the oxymuriatic acid returns to the state of muriatic acid, a quantity of that acid, combined with a portion of the

alkali, being found in the liquor. It has been concluded from these facts, in conformity to the established theory of the composition of oxymuriatic acid, that one portion of it yields oxygen to the other, one returns therefore to the state of muriatic acid, the other passes to the state of an acid containing still more oxygen than the oxy-muriatic acid, and each combines with a portion of the alkali present, so as to form neutral compounds. The acid in the latter state has, in conformity to this view, been named Hyper-oxymuriatic Acid, and its salts are denominated Hyper-oxymuriates.

This theory of course cannot be admitted, according to the hypothesis which Mr Davy has proposed of the nature of oxymuriatic acid. The existence, however, of a large quantity of oxygen in the composition of the salts named Hyper-oxymuriates, is fully established; and without admitting the existence of any acid corresponding to hyper-oxymuriatic acid in their composition, Mr Davy has supposed that these salts are ternary compounds of oxymuriatic acid, oxygen, and the base of the alkali of which they are formed. Any discussion with regard to these opposite views would, in the present state of the inquiry, be premature.

The existence of the acid named Hyper-oxymuriatic, has been inferred rather from the formation of the salt supposed to contain it, than from its being obtained in an insulated state; for in this state it does not appear that it can be procured so as to be submitted to chemical examination. When the salts supposed to contain it are submitted to the action of another acid, as the sulphuric or nitric, a greenish yellow vapour is disengaged, the liquor

around the salt becomes of an orange colour, but no sensible product can be obtained: if heat is applied to favour the action, an explosion is produced, or if this is avoided, the vapour disengaged has an intermixture of oxygen and oxymuriatic acid gases. Hyper-oxymuriatic acid, therefore, if it do exist, is unknown in a perfectly insulated state, and there are only the salts named Hyper-oxymuriates supposed to contain it, the history of which is to be delivered. From the large quantity of oxygen they contain, they act with violence on inflammable bodies, producing with them deflagration or detonation by mere trituration: they afford very pure oxygen when decomposed by heat; they produce no precipitates with metallic salts, as the muriates do; neither do they retain the power of the oxymuriates of impairing the vegetable colours.

Of these salts the Hyper-oxymuriate of Potash is best known. To prepare it, a solution of four parts of subcarbonate of potash in sixteen parts of water, from which the carbonic acid is abstracted by the action of lime, is put into the bottles of Woolfe's apparatus, and a current of oxymuriatic acid gas is passed through it, from a retort containing the materials from which this acid is disengaged: this is continued until the alkali is neutralized: the salt named Hyper-oxymuriate of Potash is deposited in scales, while a portion of muriate of potash remains in solution. The rationale of the process has been already stated: according to the theory hitherto received, the oxymuriatic acid is supposed to suffer decomposition, one portion returning to the state of muriatic acid, the other receiving the oxygen which this has yielded, and forming, by uniting with the alkali, hyper-oxymuriate of

potash: according to Mr Davy's views, the salt which has received this name is a ternary compound of oxymuriatic acid, oxygen, and potash or potassium.

Hyper-oxymuriate of potash crystallizes in scales, in needle-like crystals, or in thin quadrangular plates, white, and of a silvery lustre. It is soluble in 17 parts of water at 60°, and in two parts and a half at 212; it melts from the application of a moderate heat: when heated to redness it is decomposed, and very pure oxygen gas is expelled, amounting to more than a third of the weight of the salt. From this decomposition, Chenevix endeavoured to determine the composition both of the salt itself, and of the hyper-oxymuriatic acid which it is supposed to contain: 100 grains freed from the water of crystallization yield 38.3 of oxygen, and the residue contains 20 of muriatic acid, these being combined with 39.2 of potash, and 2.5 of water of crystallization: the two former are supposed to constitute hyper-oxymuriatic acid, the proportions of the elements of which, therefore, in 100 parts, are 65 of oxygen, and 35 of muriatic acid.

Hyper-oxymuriate of potash is decomposed by the acids. Thrown into sulphuric acid it decrepitates, the liquor acquires an orange colour, and a dense yellowish green vapour is disengaged. If heat is applied, an explosion with a vivid flash of light takes place; if the acid be diluted so as to admit of the application of heat with safety, the elastic fluid which is disengaged is a mixture of oxymuriatic acid and oxygen. The action of nitric acid is similar, but less violent. Muriatic acid is converted into oxymuriatic acid. The elastic fluid disengaged in these decompositions acts with considerable force on inflamma-

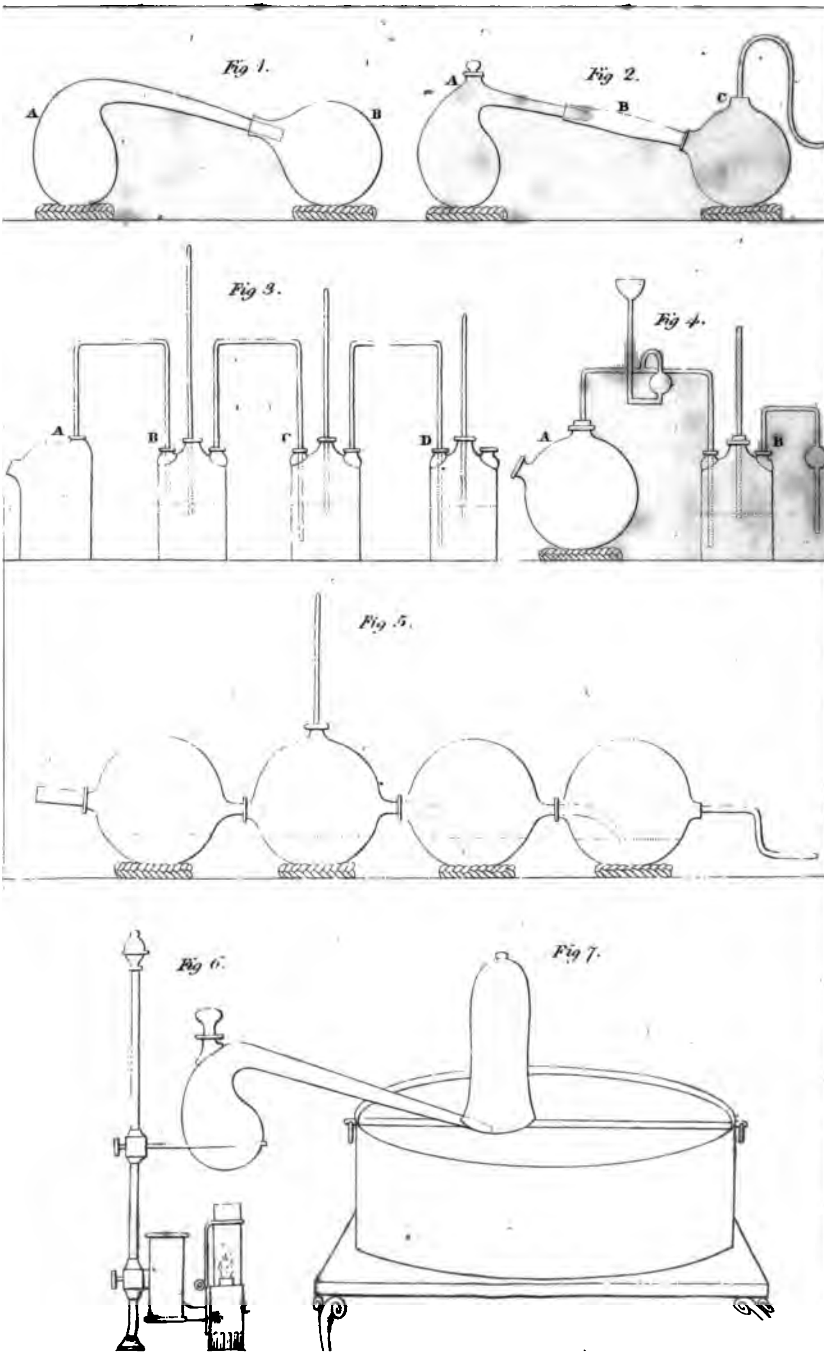
ble substances; two or three grains of the salt, for example, mixed with half the quantity of sulphur, charcoal, resins, or oils, forming mixtures which are kindled by the contact of sulphuric or nitric acid.

The salt itself acts with still more energy on inflammable bodies. If a grain or two be triturated with half its weight of sulphur or charcoal, or if the mixture in these proportions be struck forcibly, a loud detonation is produced. A similar effect is produced when several of the metals are employed; and with phosphorus the detonation is so violent, that it can be made with safety only on a very small quantity. These mixtures are also inflamed by the electric discharge and by applying heat. These effects appear to arise from the rapid combination of the oxygen of the salt with the inflammable body, and the formation in general of an elastic product.

The other hyper-oxymuriates scarcely require particular notice. The hyper-oxymuriate of soda is not so easily obtained pure as that of potash, as it is nearly of the same degree of solubility with muriate of soda, and is therefore not easily separated from it by crystallization. It crystallizes in cubes, is deliquescent, and is soluble in three parts of cold water. Hyper-oxymuriate of ammonia is formed by decomposing carbonate of ammonia by hyper-oxymuriate of lime; is very soluble in water and in alkohol, and is decomposed by a slight elevation of temperature. Hyper-oxymuriate of barytes is soluble and crystallizable, as is also that of strontites; hyper-oxymuriate of lime is deliquescent, and soluble in water and alkohol; hyper-oxymuriate of magnesia has nearly the same properties.

END OF VOL. I.

PLATE. I.



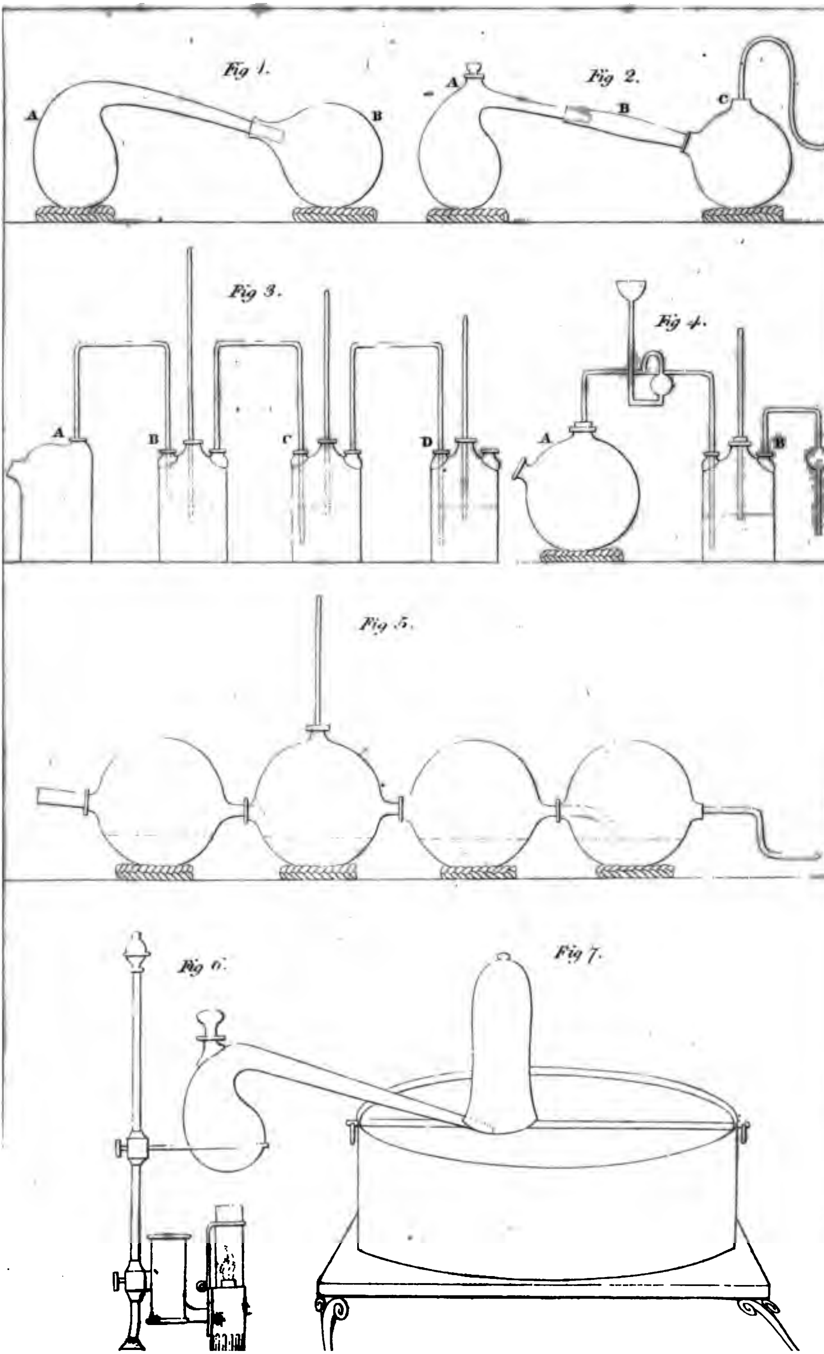
ble substances; two or three grains of the salt, for example, mixed with half the quantity of sulphur, charcoal, resins, or oils, forming mixtures which are kindled by the contact of sulphuric or nitric acid.

The salt itself acts with still more energy on inflammable bodies. If a grain or two be triturated with half its weight of sulphur or charcoal, or if the mixture in these proportions be struck forcibly, a loud detonation is produced. A similar effect is produced when several of the metals are employed; and with phosphorus the detonation is so violent, that it can be made with safety only on a very small quantity. These mixtures are also inflamed by the electric discharge and by applying heat. These effects appear to arise from the rapid combination of the oxygen of the salt with the inflammable body, and the formation in general of an elastic product.

The other hyper-oxymuriates scarcely require particular notice. The hyper-oxymuriate of soda is not so easily obtained pure as that of potash, as it is nearly of the same degree of solubility with muriate of soda, and is therefore not easily separated from it by crystallization. It crystallizes in cubes, is deliquescent, and is soluble in three parts of cold water. Hyper-oxymuriate of ammonia is formed by decomposing carbonate of ammonia by hyper-oxymuriate of lime; is very soluble in water and in alkohol, and is decomposed by a slight elevation of temperature. Hyper-oxymuriate of barytes is soluble and crystallizable, as is also that of strontites; hyper-oxymuriate of lime is deliquescent, and soluble in water and alkohol; hyper-oxymuriate of magnesia has nearly the same properties.

END OF VOL. I.

PLATE. I.



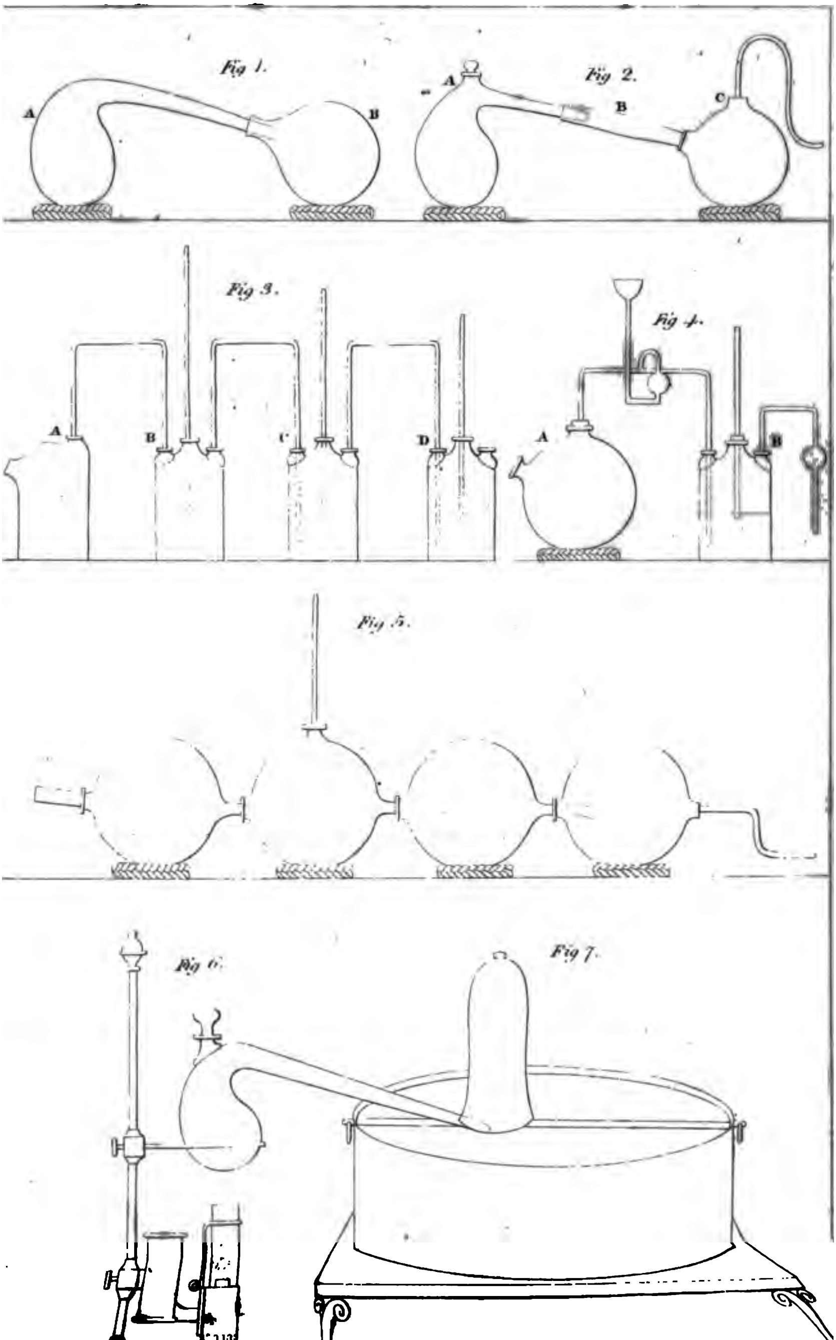
ble substances; two or three grains of the salt, for example, mixed with half the quantity of sulphur, charcoal, resins, or oils, forming mixtures which are kindled by the contact of sulphuric or nitric acid.

The salt itself acts with still more energy on inflammable bodies. If a grain or two be triturated with half its weight of sulphur or charcoal, or if the mixture in these proportions be struck forcibly, a loud detonation is produced. A similar effect is produced when several of the metals are employed; and with phosphorus the detonation is so violent, that it can be made with safety only on a very small quantity. These mixtures are also inflamed by the electric discharge and by applying heat. These effects appear to arise from the rapid combination of the oxygen of the salt with the inflammable body, and the formation in general of an elastic product.

The other hyper-oxymuriates scarcely require particular notice. The hyper-oxymuriate of soda is not so easily obtained pure as that of potash, as it is nearly of the same degree of solubility with muriate of soda, and is therefore not easily separated from it by crystallization. It crystallizes in cubes, is deliquescent, and is soluble in three parts of cold water. Hyper-oxymuriate of ammonia is formed by decomposing carbonate of ammonia by hyper-oxymuriate of lime; is very soluble in water and in alkohol, and is decomposed by a slight elevation of temperature. Hyper-oxymuriate of barytes is soluble and crystallizable, as is also that of strontites; hyper-oxymuriate of lime is deliquescent, and soluble in water and alkohol; hyper-oxymuriate of magnesia has nearly the same properties.

END OF VOL. I.

PLATE I.



7

Аш
